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## **Chemical Stabilization of Lead in Small Arms Firing Range Soils**

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**Final report**

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**ABSTRACT:** The U.S. military operates Small Arms Firing Ranges (SAFRs) at various locations in and outside the United States. The ranges are used for munitions training for military personnel. Because the ranges have been in operation for a number of years, the soils at SAFRs are contaminated with spent munitions, lead bullets, and other metal contaminants. Although SAFR projectiles contain primarily lead, copper, and antimony, lead is by far the most toxic component. As a consequence of lead-contaminated soils and the distinctive site topographies found at SAFRs, the potential for lead migration that poses risks to the environment exists. Remediation efforts are needed to mitigate lead mobility and availability.

Numerous studies have been conducted on reducing the impact of lead contaminants in the environment. This study tests chemical materials for lead stabilization that are economical and readily adaptable to field application at SAFRs. The study evaluates the effectiveness of iron and phosphate chemicals as in situ treatments for reducing lead mobility at SAFRs.

Two leaching tests were developed. One test evaluated treatment effectiveness during leaching at the natural soil pH, and the second leach test was conducted at a lower, acidic, pH to estimate the long-term effects of lead leaching at SAFRs.

The study showed that phosphate amendments were more effective than iron amendments in stabilizing lead in SAFR soils.

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# Preface

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This report describes the results of testing chemical compounds for in situ stabilization of lead in soils at Small Arms Firing Ranges (SAFRs). This study was conducted by the Environmental Laboratory (EL), Vicksburg, MS, U.S. Army Engineer Research and Development Center (ERDC), under the Environmental Quality and Technology Program, Inorganics in Soils Focus Area, Dr. M. John Cullinane, Jr., EL, Program Manager.

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Commander and Executive Director of ERDC was COL James R. Rowan, EN. Director was Dr. James R. Houston.



# 1 Introduction

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## Background

The reclamation of historically contaminated sites on military facilities is a primary goal of the Department of Defense. Military ranges used for training exercises typically contain unexploded ordnances, explosive residues, and shell fragments that may become environmental concerns. These ranges include mortar and artillery ranges, grenade ranges, bombing ranges, and small arms firing ranges (SAFRs). This effort specifically addresses the SAFRs that are found at nearly all military facilities and are essential to weapons training and the mission of the military. A typical SAFR is designed with a large impact berm or earthen backstop for trapping bullets fired during the training exercises (Figure 1).

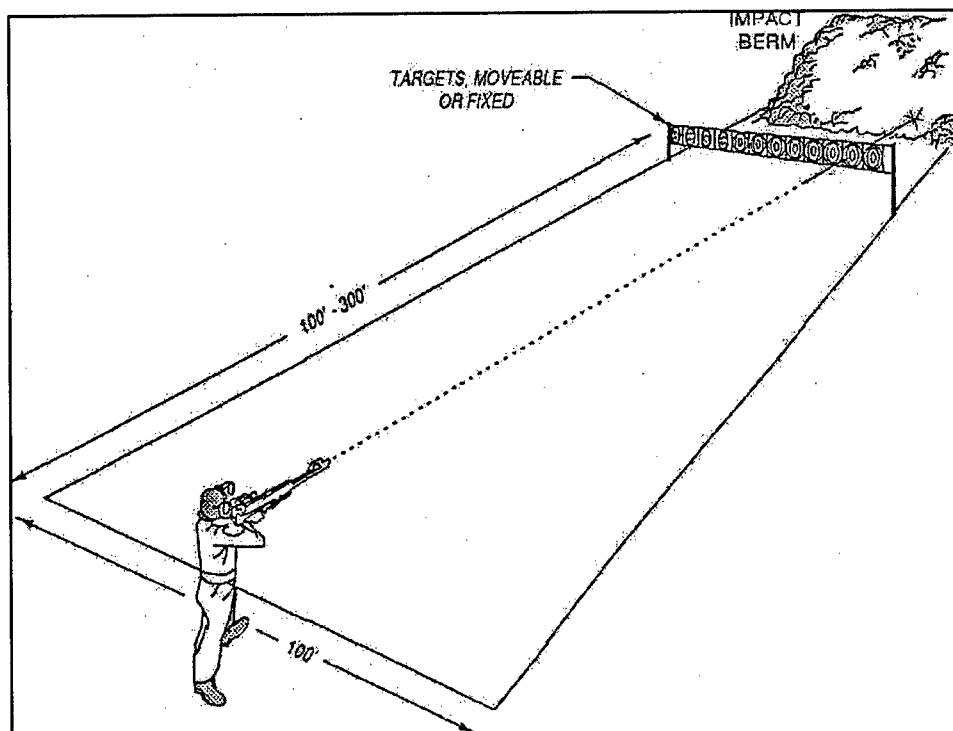


Figure 1. Typical small arms firing range

Through years of use, the soils in these berms accumulate high concentrations with lead and other metals from the spent munitions. The lead is

found as spent bullets, shattered fragments, small particles, and lead smears on larger sand grains. The spent bullets and larger fragments can be removed and recycled by simply screening the material. The remaining smaller particles and sand grains must be treated or removed to prevent the leaching or migration of lead into adjacent soils and groundwater (U.S. Environmental Protection Agency (USEPA) 2001a). Copper and antimony are also commonly found at these sites but typically are less an environmental hazard than lead.

The lead and other contaminants can migrate into surrounding soils and waters by horizontal erosion by winds and runoff during storm events, or by leaching into the groundwater in infiltrating rainfall (Figures 2, 3, and 4).

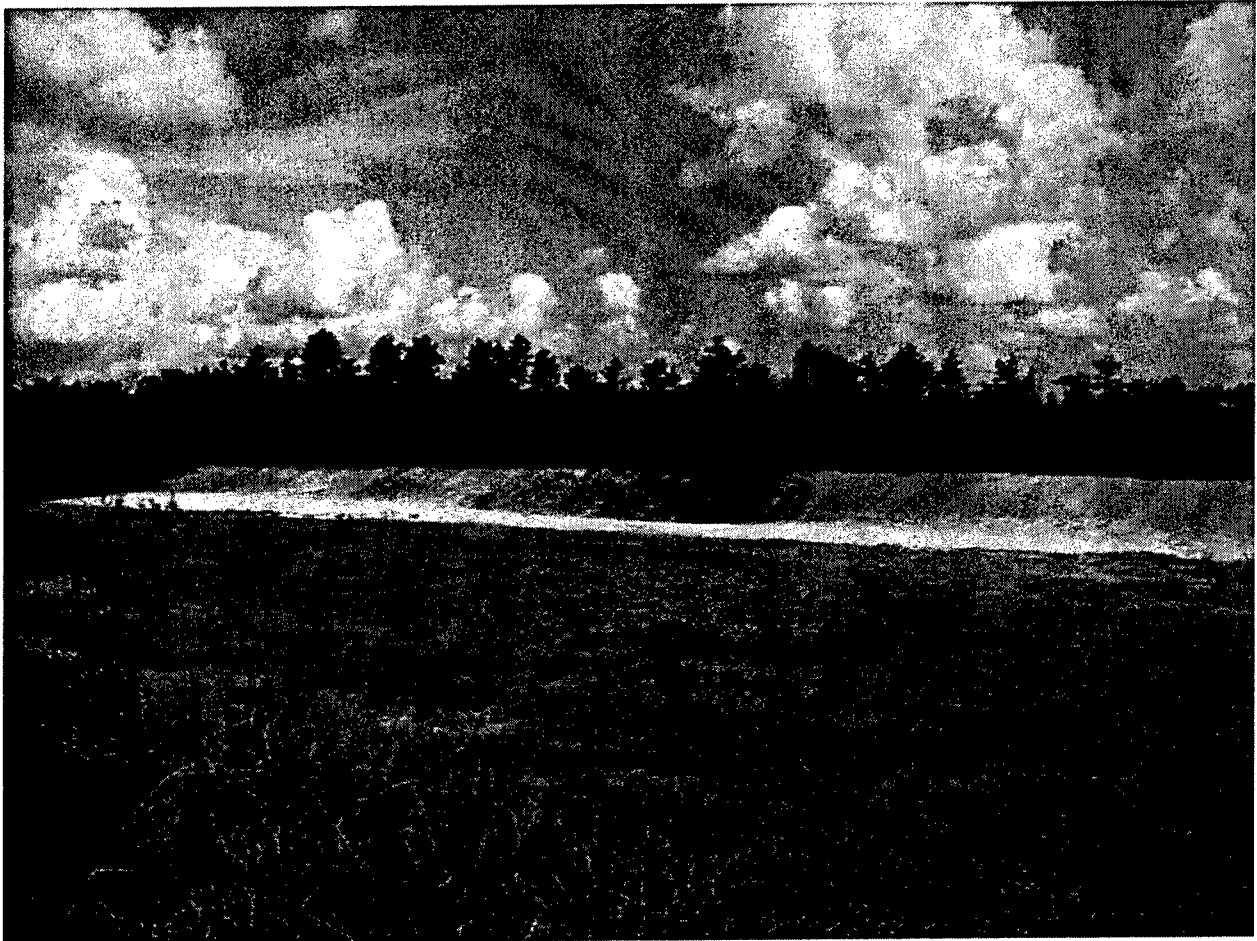


Figure 2. Inactive SAFR impact berm



Figure 3. Spent projectiles trapped in SAFR berm

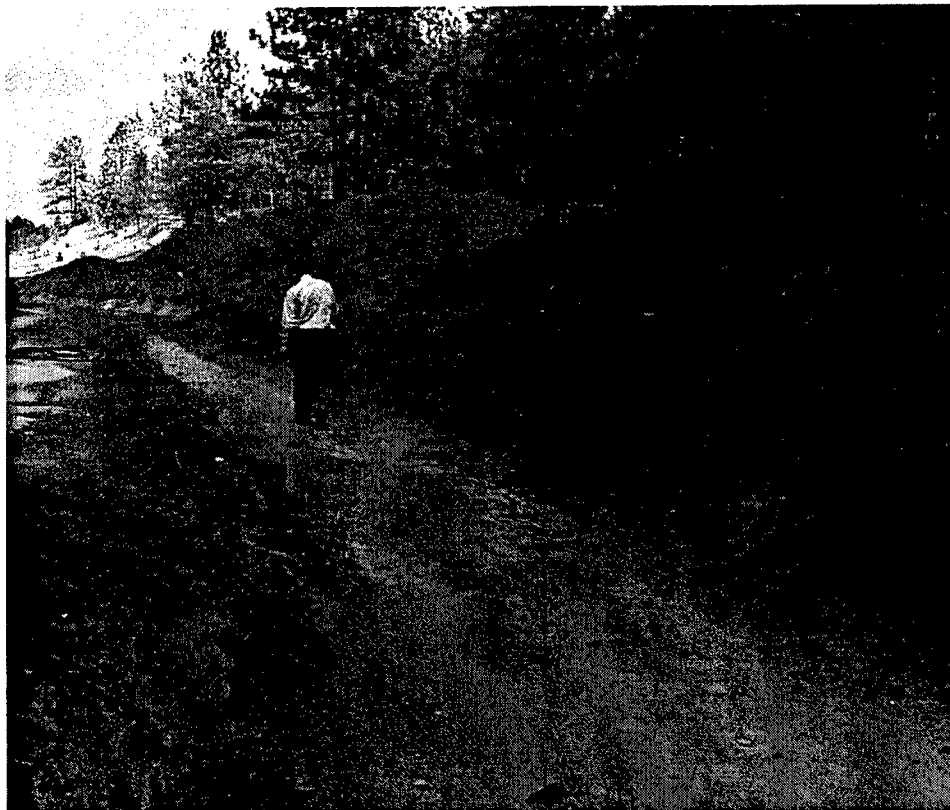


Figure 4. Contaminant migration from washout area at a SAFR berm

Migration rate at any given site is determined by the characteristics of the local soil, site topography, metal solubility, precipitation events, and the occurrence of freeze-thaw cycles. A thorough discussion of contaminant migration and transport may be found in Selim et al. (1990), Rubin (1993), and Myers et al. (1996).

Small arms firing range soils have typically been treated by solidifying the soil with cement and/or fly ash to prevent metal migration, sieving and soil washing to remove lead contamination (Naval Facilities Engineering Service Center 2002), or removal to hazardous waste landfills (USEPA 2001a). These treatment methods can be very expensive and result in additional contaminated materials. Several authors have conducted studies indicating that the potential environmental impact of lead-contaminated soils is strongly affected by lead bioavailability, i.e., lead solubility (Zhang and Ryan 2000; Hettiararchi and Pierzynski 2000). Reducing lead solubility and thus its bioavailability greatly minimizes the adverse effects of lead-contaminated soils on the environment.

Several studies have suggested that in situ treatment of lead-contaminated soils might be accomplished by incorporating inexpensive amendments into the soil (Berti and Cunningham 1997; USEPA 2000; Zhang and Ryan 2000; Stanforth and Qiu 2001). This report discusses tests of several soil additives that have the potential for preventing lead migration and bioavailability by reacting with, precipitating, and stabilizing the lead.

## Lead Solubility and Bioavailability

Lead is a naturally occurring, grayish, soft metal found naturally in the earth's crust. Lead in soils may exist in various forms: water soluble (dissolvable lead); exchangeable (displaceable by other cations); adsorbed or chemically adsorbed; chelated; complexed; and insoluble, precipitated lead (Ma and Rao 1997; Lambert et al. 1997). Soluble, exchangeable, and adsorbed forms of lead have a higher bioavailability and mobility than less soluble forms.

The solubility of some selected lead minerals is shown in Table 1.

<b>Table 1</b> <b>Solubility Products of Selected Pb Minerals</b>		
<b>Mineral</b>	<b>Formula</b>	<b>Log K<sub>sp</sub><sup>1</sup></b>
Lead chloride	PbCl <sub>2</sub>	-4.8
Anglesite	PbSO <sub>4</sub>	-7.8
Cerussite	PbCO <sub>3</sub>	-12.8
Pyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	-84.4
Hydroxypyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	-76.8
Fluoropyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	-71.6
Bromopyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Br	-78.1
Corkite	PbFe <sub>3</sub> (PO <sub>4</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub>	-112.6
Hinsdalite	PbAl <sub>3</sub> (PO <sub>4</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub>	-99.1
Plumbogummite	PbAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> •H <sub>2</sub> O	-99.3
<sup>1</sup> Log of the solubility product at 25° C. Cited in Traina and Laperche (1999).		

The lead phosphate minerals have very low solubilities compared to the solubility of  $\text{Ca}(\text{OH})_2$ , which has a log solubility product of -5.2, or calcite or aragonite ( $\text{Ca}(\text{CO}_3)$ ), -8.1. The several forms of pyromorphite are 60 to 70 orders of magnitude less soluble than either calcium minerals in water at 25 °C. Other studies investigated naturally occurring and synthetic iron and phosphate chemicals as materials for lead immobilization in the environment. Ma and others (1992, 1993, 1994a, 1994b, 1995, and 1997) conducted extensive studies of the ability of phosphate materials to immobilize lead in soils and sediments. Their results show the potential of the phosphate minerals, apatite and hydroxyapatite, and other phosphate reagents to decrease lead solubility and bioavailability substantially. The studies showed that these materials were effective even in the presence of large concentrations of other interfering metal ions, aluminum, cadmium, copper, iron ( $\text{Fe}(\text{II})$ ), nickel, and zinc (Ma et al. 1994b), or in the presence of levels of the cations nitrate, chloride, fluoride, sulfate, and carbonate (Ma et al. 1994a).

Laboratory tests evaluating the effect of a number of materials on lead solubility were made by Berti and Cunningham (1997). Three soils with lead concentrations ranging from 1,200 to 3,500 mg/kg were treated with various levels of  $\text{KH}_2\text{PO}_4$ , limestone, iron oxyhydrides, gypsum, sulfur, organic amendments, and Portland cement. Following an extraction procedure, three treatments—6 percent iron oxyhydrides, 0.1 percent  $\text{KH}_2\text{PO}_4$ , and 12.6 percent Portland cement—reduced leachable lead concentrations in the extracts to below the USEPA regulatory level of 5.0 mg/kg.

Chen et al. (1997) investigated the effect of varying pH on the sorption behaviors of aqueous lead, cadmium, and zinc in the presence of a form of apatite found in North Carolina. They found that heavy metals were immobilized to a large extent via formation of insoluble pyromorphites. Ma et al. (1993) reacted synthetic hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ], calcium biphosphate [ $\text{CaHPO}_4$ ], and fluoroapatite (a natural apatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ) with aqueous lead, resin-exchangeable lead, and lead-contaminated soil. All three sources of calcium phosphate were effective in immobilizing the lead in all three systems. Examination of the resulting solids by various techniques indicated conversion of lead to insoluble pyromorphite [ $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ ]. Ryan et al. (2001) found the formation of chloropyromorphite in lead-contaminated soils amended with hydroxyapatite. Additional studies (Laperche et al. 1996, 1997) further indicated that phosphate and apatite amendments were effective in immobilizing lead.

Shi and Erickson (2000) have developed mathematical models that include adsorption, diffusion, and reaction to describe the transformation of lead contaminants to pyromorphite in single particles, aggregates, and soil beds. Principal factors controlling the time of remediation were identified. The contaminated aggregate model describes the effect of initial contaminant concentration, diffusion coefficient, and aggregate diameter on the time of remediation.

The risk to humans and the environment associated with lead contamination depends upon how readily it is absorbed into the organism, i.e., its bioavailability. Historically, remediation decisions have been based upon an assumed bioavailability level of lead of 30 percent for all forms of lead in the soil

(USEPA 2001b). However, USEPA has realized that lead bioavailability varies greatly depending upon its form in the soil. Hydroxyapatite has proven to be an effective source of phosphorus for binding with and reducing bioavailable lead in contaminated soil to below the USEPA action level. Furthermore, lead in water supplies can be bound by adding phosphate minerals to form pyromorphite from which lead is not released when ingested by humans or other animals (Berti and Cunningham 1997). In studies of 20 lead-contaminated soils at mining sites by Region 8, USEPA (2000), lead sulfates were found to have relatively low bioavailability (<25 percent bioavailable) compared to lead carbonates (>75 percent bioavailable). Lead carbonate may pose a potential health concern to biological systems due to its high bioavailability. The bioavailability of lead then is determined by its chemical state in the soil or sediment.

In the simulated intestinal phase (pH 2.5) of the physiologically based extraction test (PBET), lead in solution was reduced by 72 percent in a contaminated soil treated with a 10 percent dose of a high-iron-containing industrial byproduct (Berti and Cunningham 1997). The PBET simulates the action of digestive fluid in the stomach on metal availability. Hettiarachchi and Pierzynski (2000) showed that triple phosphate addition to contaminated soils reduced lead content of PBET extracts. The addition of manganese oxides increased the effectiveness of the added phosphate in their studies. Using earthworms as test organisms, Pearson et al. (2000) found that earthworms grown in phosphate-amended soils had significantly reduced lead levels, while zinc and cadmium levels in mixture experiments were not affected. X-ray diffraction analysis indicated that pyromorphites were formed reducing the solubility and bioavailability of the lead. In contrast, the addition of organic matter increased the bioavailability of lead.

An apatite amendment to contaminated soils also lowers the bioavailability of lead to plants growing on the soil. Laperche et al. (1997) have shown that the lead content in shoot tissue decreased as the quantity of added apatite increased. Although lead content in the shoots was reduced to a great extent, lead accumulated in the roots through the formation of pyromorphite on the root surfaces. The levels of lead, cadmium, and zinc in swiss chard and sudax plant tissues were reduced in the presence of soluble phosphorus (Hettiarachchi and Pierzynski 1997). They also found that addition of manganese oxide increased the effectiveness of the added phosphate. Bentonite and steelshot soil amendments produced a reduction in lead content in lettuce and bean plants grown in lead-contaminated soils (Geebelen et al. 2002). Cyclonic ash, lime, compost, and hydroxyapatite reduced the amount of  $\text{Ca}(\text{NO}_3)_2$  extractable lead, indicating a reduction in lead phytoavailability.

The successful remediation of lead-contaminated SAFR soils by in situ immobilization in iron or phosphate minerals using inexpensive reagents and equipment appears to be a viable option. This potential is the focus of this investigation.

## Study Objectives

The U.S. Army Engineer Research and Development Center (ERDC) conducted this study to provide strategies for effective and economical remediation and management practices at SAFRs. This study was specifically undertaken

- a.* To research and identify potential materials for in situ stabilization and immobilization of lead in soils from SAFRs.
- b.* To evaluate the selected candidate materials for their effectiveness in lead immobilization in test soils.
- c.* To develop an effective remediation strategy to reduce the risk of offsite lead migration from contaminated soils at SAFRs.

## 2 Experimental Design and Test Development

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This study of the effects of selected additives on the solubility and mobility of lead in SAFR soils was conducted in three phases. The first phase involved soil preparation, physical and analytical testing of the soils, and preparation of soils spiked with a lead compound. The second phase involved establishing and testing an aggressive soil leaching procedure. The third phase entailed development of the chemical treatment protocol to evaluate the effectiveness of the selected additives in stabilizing the lead in the soils. Detailed protocols for the procedures used are given in Appendix A.

Four lead-contaminated soils from SAFRs on military installations were selected for the study. In addition, two uncontaminated soils spiked with three levels of lead were included to further refine the experiment. Each of the soils was treated with three levels of iron and phosphate additives to evaluate their effectiveness in rapidly reducing the level of leachable lead in the soils. The following additives were selected for evaluation in the study:

- Granular and colloidal zero-valent iron.
- Hydroxyapatite powder  $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ .
- Calcium phosphate  $[\text{Ca}_3(\text{PO}_4)_2]$ .
- Sodium phosphate  $[\text{Na}_3(\text{PO}_4)]$ .
- Potassium phosphate  $[\text{K}_3(\text{PO}_4)]$ .
- Ammonium phosphate  $[(\text{NH}_4)_3(\text{PO}_4)]$ .

### Soil Selection and Characterization

Two of the SAFR soils were collected for this study from U.S. Army sites at Camp Keller in Wiggins, MS, and at Fort Polk, LA. The two other SAFR soils were collected from sites at the U.S. Coast Guard Communication Center in New Orleans, LA, and the U.S. Coast Guard Integrated Support Command in Kodiak, AK. The bulk physical properties of the SAFR soils from Fort Polk, New



Orleans, and Kodiak soils are reported in detail in Bricka et al. (1999). The SAFR soil from Camp Keller was characterized for this study.

The two soils used for the spiked lead addition were a kaolin soil composed of almost pure kaolinite, a hydrous aluminum silicate mineral ( $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 \cdot \text{SiO}_2$ ), which contained 0.1 to 4 percent free silica ( $\text{SiO}_2$ ). This material was purchased directly from Georgia Kaolin Company, now the Feldspar Corporation, Atlanta, GA.

The second soil selected for spiking with lead was a previously studied reference soil, designated WES, that was collected from an area in Warren County, MS, near Vicksburg, MS, site of ERDC. This soil was a Mississippi loess soil that was deposited on the Pleistocene Mississippi-Ohio Valley flats and was composed of well-sorted yellowish-brown, clayey silt. Iron made up over 20 percent of the bulk of the fines, magnesium over 2 percent, and calcium around 1.5 percent.

From the testing of replicate soil samples, the presence of pure metallic lead in bullets and bullet fragments in the SAFR soils caused widely variable and inconsistent analytical results and thus precluded the preparation of consistent and homogenous samples from the field soils. Consequently, all of the procedures in this study were performed after the spent bullets and bullet fragments had been removed from the soils by sieving, and after the remaining soil was dried, sieved, and ground to a fine powder. The removal of the bullets and fragments lowered the levels of lead in the firing range soils but made possible the use of replicate samples with consistent lead content. Large-scale testing and sampling of the soils containing the bullet fragments and spent munitions is planned in a later study.

The physical characteristics of the soils were determined using standard laboratory procedures. Moisture content and specific gravity were determined according to the American Society of Testing and Materials (ASTM) procedures D2216 (ASTM 1998) and D854 (ASTM 2002), respectively. Grain size analysis followed the procedures in ASTM C136 (ASTM 2001).

Chemical analyses were performed on the processed soils according to the standard analytical methods listed in Table 2. Chemical characterization of the powdered soil samples included lead concentration, pH, and oxidation-reduction potential (ORP).

## Sample Preparation

Soils collected from the firing range sites were dried and screened through a 10-mesh (1.7-mm) sieve to remove large particles and bullet fragments. The screened soils were then ground to a fine powder using a Pulverisette #7 Soil Grinder, and re-screened through a 120-mesh (125- $\mu\text{m}$ ) sieve according to the procedures outlined in Appendix A, Section 1.

<b>Table 2</b> <b>Chemical Methods and Detection Limits for Soil Analyses</b>			
Parameter	Method	Detection Limit	
		Water, mg/L	Soil, mg/kg
pH	SW-846-9045C (soil) <sup>1</sup>	NA <sup>3</sup>	NA
Oxidation-Reduction Potential	Standard Methods <sup>2</sup>	NA	NA
Lead	SW-846-7420 <sup>1</sup>	1	1
	SW-846-6020	<0.00002	<0.00002
<sup>1</sup> USEPA 1999. <sup>2</sup> Standard Methods for the Examination of Water and Wastewater (American Public Health Association 1998). <sup>3</sup> NA = Not applicable.			

Preparation of the WES and kaolin soils followed the same procedures as the firing range soils (Appendix A, Section 1). Samples of the powdered WES and kaolin soils were spiked with aqueous solutions containing 500, 1,000, and 2,000 mg/L of lead as lead nitrate (Appendix A, Section 2). An aliquot of stock solution (100,000 mg/L) was added to a measured weight of dried soil and mixed. After 24 hours of agitation, the samples were centrifuged to separate the liquid fraction. The solids were then rinsed with distilled, deionized water (DDI) three or four times to remove all the lead that was not adsorbed onto the solids. The volume of the liquid rinse samples was measured and the lead concentration determined. The solid components were dried in an oven at 110 °C for 24 hours and then rescreened through a 120-mesh sieve.

## Soil Leaching Procedures

Two leaching protocols were developed to measure the loss of lead from the soils before and after the addition of the stabilization additives. A leaching equilibrium test was conducted to provide data on lead removal from the untreated soils.

### Leaching without pH adjustment

At the “natural,” unadjusted soil pH, 50 ml of DDI water was added to a set of 5-g samples contained in polyethylene bottles. The samples were placed on a rotary tumbler and mechanically agitated end over end for the length of the test period. At the conclusion of the leaching period the aqueous and solid components were separated. This procedure mimics the leaching process that naturally occurs at the lead-contaminated sites due to repeated rainfall events.

### Aggressive leaching with pH adjustment to pH 3.0

A second, more aggressive leaching was also developed to better estimate the effects of leaching over a period of years. In this procedure, leaching tests were conducted after adjusting the pH of the leaching mixture to  $3.0 \pm 0.5$  with 0.2-M nitric acid. To another set of 5-g soil samples, 25 ml of DDI water and 5 ml of

0.2-M nitric acid were added. The bottles were then sealed and tumbled. During the leaching process the pH of the samples was tested and maintained by incremental addition of 1 ml of 0.2-M nitric acid. Approximately 2 hours before the end of the leaching test, additional DDI water was added to bring the volume of liquid to 50 ml. The liquid was then separated by centrifugation and filtration, and analyzed for lead content.

The lower pH value increases lead solubility and mobility, and provides additional data for evaluating the long-term effectiveness of chemical amendments in stabilizing lead-contaminated soils. If leachate concentrations of lead remain below the USEPA action level after a period of agitation at pH 3, the likelihood of loss of leachable lead from the treated sample over the long term would be minimal.

### **Determining leaching time necessary for leachate equilibrium**

A preliminary leaching procedure was carried out to find the length of time necessary for the equilibration of the soil lead concentration with the liquid leachant phase. Triplicate samples of all soil types at natural pH and pH 3.0 were mixed and tumbled for 0.8, 1, 3, 5, 7, and 10 days.

## **Leaching Protocols and Amendment Addition**

The effectiveness of the chemical treatment in stabilizing lead in the soils was determined by comparing lead concentration in leachates from amended soils with those in the control soils without amendment. The additives selected for ability to stabilize the lead in the test soils were two grades of zero-valence iron—granular and colloidal—and the phosphate-containing materials—hydroxyapatite powder, calcium phosphate, sodium phosphate, potassium phosphate, ammonium phosphate, and phosphoric acid. All additives were mixed into the test soils at three levels: 1, 3, and 5 percent by weight. Duplicate samples were prepared and tested in all cases. The detailed protocol for preparing the test samples is described in Appendix A, Section 4.

### **Preparation of samples for leach testing at natural pH**

A 50-ml aliquot of DDI water was added to the dry materials in each sample bottle. The bottles were then tumbled for 20 minutes after which the pH and ORP of the samples were measured with a pH/ORP meter. The sample bottles were then replaced on the rotary tumbler for an additional  $72 \pm 2$ -hour leaching period. The samples were then centrifuged for 30 minutes at 6,000 rpm. The supernatant was filtered through a 0.45- $\mu$ m filter in a vacuum syringe filter. After filtration, the pH and ORP were remeasured. Nitric acid was added, dropwise, to the filtered supernatant sample to preserve the samples at pH <2. The samples were stored at -4 °C until they could be analyzed for lead content by Atomic Absorption Spectroscopy, Inductively Coupled Argon Plasma, or Inductively Coupled Plasma-Mass Spectrometry as appropriate.

### **Preparation of samples for leach testing at pH 3**

After the soil samples with the additives were prepared as described, 25 ml of DDI water was added to the dry materials in each sample bottle. Then 5 ml of 0.2-M Ultrex nitric acid was added to the bottle and the bottle shaken briefly to mix the materials. The pH of the sample was then tested with pH paper. If necessary, additional nitric acid was added in 1- to 2-ml increments until the pH of the sample mixture was lowered to  $3.0 \pm 0.5$ . The bottles were then tumbled for 24 hours at which time the pH and ORP were again measured and, if necessary, additional nitric acid was added to reduced the pH to  $3 \pm 0.5$ . The same procedure was carried out after 48 hours of tumbling to maintain the pH at the test level. After 72 hours, volumes were brought to 50 ml. The samples were then centrifuged, filtered, and preserved in a manner similar to the test samples run at natural pH.

### **Chemical amendment addition**

All seven amendments were tested for lead contamination. Tests were conducted at both the natural soil pH and after pH adjustment to  $3.0 \pm 0.5$  with dilute nitric acid. In all cases, the lead concentration in the leachates from the chemical amendments was at or below the control blanks.

The iron and phosphate chemical amendments were applied at 1, 3, and 5 percent (amendment weight /dry soil weight) to the SAFR soils and the spiked WES and kaolin soils. Measured amounts of the dried and powdered amendments (50, 150, and 250 mg) were mixed with 5 g of each of the soils in polyethylene bottles. The samples were tumbled and mixed for 3 days at their natural, unadjusted pH, and at pH 3.0 as described previously. For each treatment, untreated (0 percent chemical addition) soil samples were carried through the same procedures at both pH conditions. At the end of 3 days, the aqueous and solid phases were separated by filtration and the aqueous phase analyzed for lead, ORP, and pH.

The success of the chemical treatments in stabilizing lead in the soils was determined by comparing lead concentrations of the chemically treated soils to those of the untreated soils and by the lead concentration in the leachates from the treated samples. To be successful, the leachate concentrations should be less than 5.0 mg/L as proscribed by the USEPA Toxicity Characteristic Leaching Procedure (TCLP) (USEPA 2002). Ideally the leachate concentrations would be below the USEPA drinking water limits for lead, 0.015 mg/L.

### **Analytical Procedures**

The untreated SAFR soils and the lead-spiked WES and kaolin soils were digested according to SW-846 Method 3051 (USEPA 1999). The digested soil samples and the liquid samples containing greater than 1 mg/L lead were analyzed for lead content by SW-846 Method 7420 (USEPA 1999) Flame Atomic Absorption Spectroscopy using a Perkins Elmer 5100 Flame Atomic

Absorption Spectrophotometer. Lead quantification for the liquid samples containing less than 1 mg/L lead was according to SW-846 Method 6010B (USEPA 1999) Inductively Coupled Plasma on a Perkins Elmer Optima 3000 or by SW-846 Method 6020 (USEPA 1999) Inductively Coupled Plasma-Mass Spectrometry on a Perkins Elmer Sciex 6000.

Each analytical run included triplicate DDI water method blanks and triplicate quality control (QC) reagent standards at 80 mg/L. The percent standard deviation of the reagent QC standards was typically less than 1 percent. The values of the method blanks were subtracted from the measured values.

## 3 Results and Discussion

### Soil Characteristics

The moisture content of the powdered soils varied from a high of 2.3 percent to a low of 0.2 percent. Grain size analysis of the processed soils showed that 95 percent of the particle sizes were smaller than 0.125 mm (120 mesh). The larger 5 percent fraction ranged in size from 0.15 to 0.18 mm.

The lead content of the powdered, screened, and dried soils is illustrated in Figure 5, and the values are listed in Table 3. The lead content of the SAFR soils ranged from a high of 10,100 mg/kg soil for the Kodiak soil to a low of 1,012 mg/kg for the New Orleans soil. The kaolin and WES soils had lead concentrations of less than 100 mg/kg in the native soils to over 2,500 mg/kg in the highest lead-spiked soils. The initial pH and ORP values for each soil are also listed in Table 3.

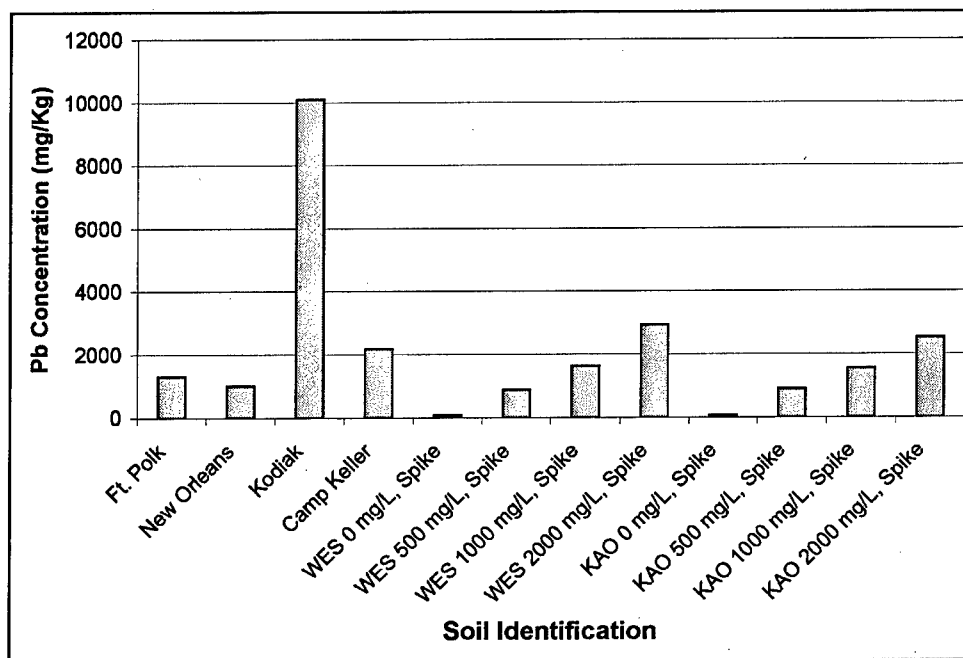


Figure 5. Lead concentration in test soils

The soil pHs were all between about pH 5.38 and 6.19 except for the New Orleans soils, which had a pH of about 7.5. The ORP values ranged from 237 to 409.

<b>Table 3 Selected Properties of Lead-Contaminated Test Soils</b>			
<b>Test Soil, mg/kg Lead</b>	<b>pH</b>	<b>ORP mV</b>	<b>Lead Concentration, mg/kg</b>
Fort Polk 1,289	5.81	237	1,289
New Orleans 1,012	7.46	278	1,012
Kodiak 10,100	6.19	293	10,100
Camp Keller 2,174	5.38	324	2,174
WES 81	5.73	409	81
WES 876	5.79	394	876
WES 1,630	5.72	307	1,630
WES 2,930	6.00	289	2,930
Kaolin 69	5.88	346	69
Kaolin 896	5.83	314	896
Kaolin 1,549	5.59	330	1,549
Kaolin 2,526	5.60	322	2,526

### **Comparison of lead content in spiked soil samples determined by direct analysis with that calculated by mass balance**

Figure 6 compares the theoretical lead concentration for the spiked WES and kaolin soils to the lead concentration found by direct analysis of the soils. The mass balance calculations using the total lead content of the DDI soil washings determined the theoretical amount of bound lead that remained on the spiked soils. The lead spike solutions containing 500, 1,000, and 2,000 mg/L lead as lead nitrate corresponded to theoretical lead concentrations in the soils of 833, 1,666 and 3,333 mg lead/kg soil, respectively.

The lead content found by analysis of the digested soils samples were 876, 1,630, and 2,931 mg/kg for the spiked WES soils and 896, 1,549, and 2,526 mg/kg for the spiked kaolin soils. The data in Figure 6 plot the spiked soil concentrations after subtracting the original lead content of the WES (81 mg/kg) and the kaolin (69 mg/kg) soils from their measured values. The average mass balance recovery for lead in the spiked WES and kaolin soils was 96.7 percent.

Application of the spike solutions resulted in 95, 93, and 86 percent lead absorption onto the WES soil, respectively, and 99, 89, and 74 percent lead adsorption to the kaolin soil, respectively. The data indicate a close correlation between the measured and theoretical lead concentrations in the spiked soils.

### **Leachate equilibration results**

Preliminary leaching tests were run over 10 days to determine the time necessary for the lead in the leachates to reach equilibrium with the soils. Lead concentration in leachates conducted at the natural soil pH for the SAFR soils

and the WES and kaolin lead-spiked soils are shown in Figures 7, 8, and 9, respectively. With the exception of the Kodiak soil results on Day 1 (Figure 7), the lead concentrations in the leachates had equilibrated by Day 3. Also, leachate lead concentrations reached 95 percent of their maximum values on Day 3 for both the spiked WES and kaolin soils (Figures 8 and 9). In a few cases after Day 3, the concentrations trended upward and attained their maximum values on Day 7. The results show that very low levels of lead were leached from the soils at the natural pH of the soil. Lead concentrations were below 1 mg/L for all of the soils tested at all time periods.

The lead concentrations in leachates taken at different leaching periods from the accelerated leaching tests conducted at pH 3 are shown in Figures 10, 11, and 12. Leachate concentrations of lead in the samples maintained at pH 3 illustrate the much higher solubility and mobility of the lead at the lower, acidic pH. Lead concentrations increased from 100 to 1,000 times those in leachates eluted with DDI water at natural soil pH.

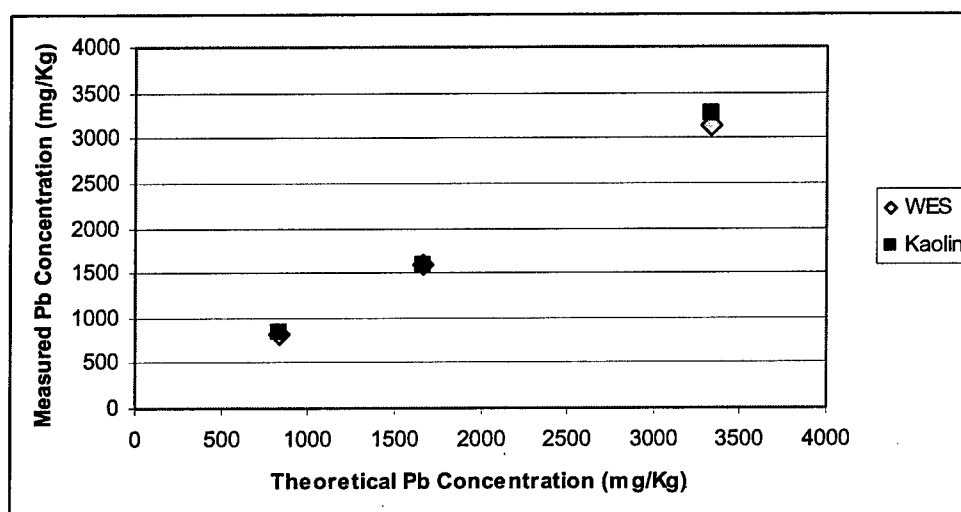


Figure 6. Comparison of measured lead concentration in spiked soils with that calculated by mass balance

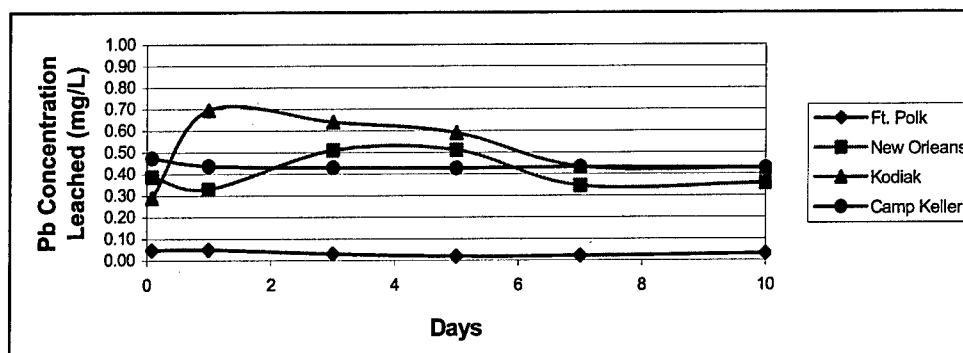


Figure 7. Lead concentration in leachates from SAFR soils at natural pH



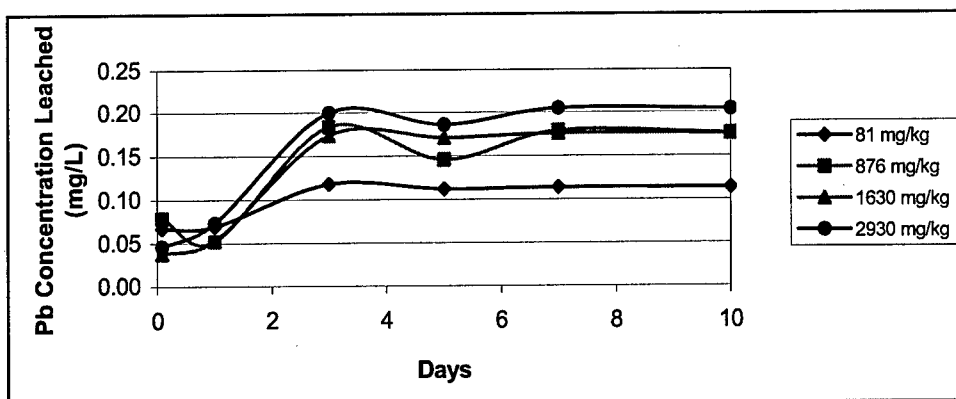


Figure 8. Lead concentrations in leachates from spiked WES soils at natural pH

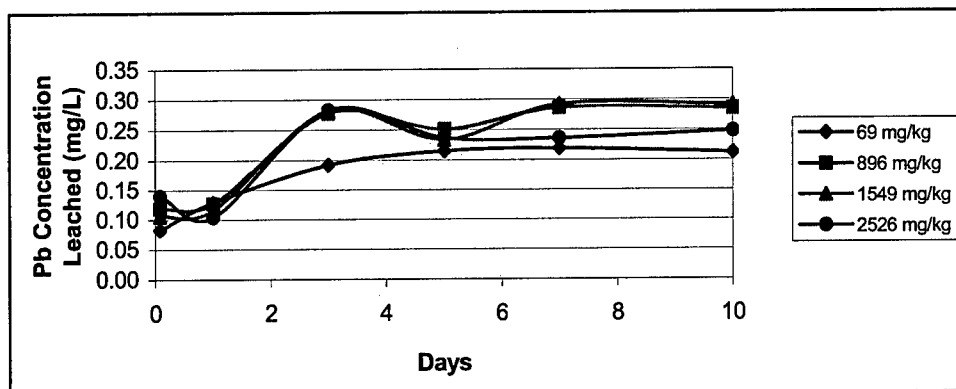


Figure 9. Lead concentration in leachates from spiked kaolin soil at natural pH

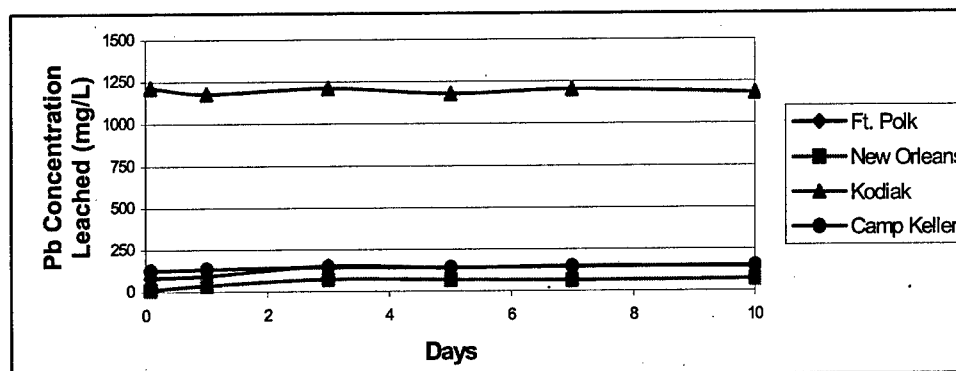


Figure 10. Lead concentrations in SAFR soils at pH 3.0

Maximum lead concentration values resulting from leaching the Fort Polk, New Orleans, Kodiak, and Camp Keller soils at pH 3 were 152 mg/L on Day 3, 74 mg/L on Day 3, 1,216 mg/L on Day 1, and 150 mg/L on Day 7, respectively. In almost all cases, lead concentrations had reached their equilibrium values by Day 3. In the two instances in which concentrations were not attained on Day 3, lead concentrations were only 5 mg/L higher than the Day 3 values. This value is well within the quality control limits of the analytical method.

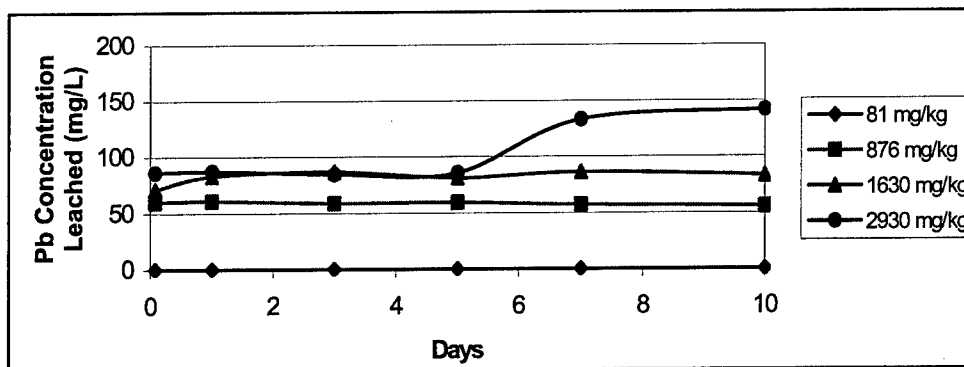


Figure 11. Lead concentrations in leachates from spiked WES soils, pH 3.0

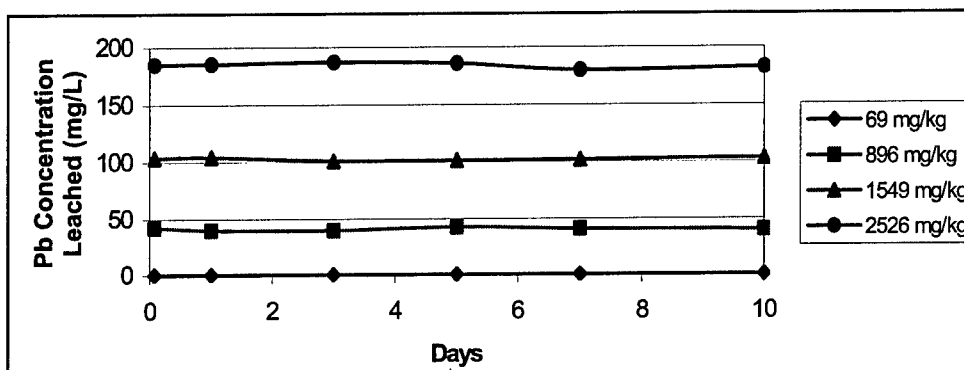


Figure 12. Lead concentrations in leachates from spiked kaolin soils at pH 3.0

The highest lead concentration results at pH 3 for the 500-, 1,000-, and 2,000-mg/L spiked WES soils were 59 on Day 3 versus 61 on Day 1; 87 on Day 3; and 85 on Day 3 versus 141 mg/kg on Day 10, respectively. Again, with few exceptions, maximum leachate lead concentrations were attained on Day 3 for the WES soils. The results for the 2,000-mg/L spiked WES soil could indicate that the 2,000-mg/L lead-spike solution exceeded the capacity of the WES soil to bind lead.

Leachate lead concentration results at pH 3 on Day 3 for the 500-, 1,000-, and 2,000-mg/L spiked kaolin soils were 40, 101, and 187 mg/kg, respectively. Lead concentrations were only slightly higher for the two soils (500 mg/L and 1,000 mg/L) that did not reach peak concentrations on Day 3. The leachate lead concentrations for those two soils differed from the Day 3 results by only 3 mg/kg.

With the exception of the 2,000-mg/L spiked WES soil, the differences in maximum leachate concentrations from Day 3 for all the soils tested were well within the established criteria of  $\pm 20$  percent relative percent difference for the analytical method. A 3-day leaching period was selected for all further testing.

## Effects of pH on lead leaching rates of untreated, control soils

The contaminated and spiked soils were leached both without pH adjustment and with pH adjusted to  $3.0 \pm 0.5$ . Final pH values for the soil slurries for all tests are listed in Appendix B. Leaching at the more acid pH resulted in the loss of significantly more lead than leaching the soils with DDI water at their "natural" pHs. The liquid-to-solid ratio in all cases was 10:1.

This protocol differs from, and is more aggressive than, the USEPA's TCLP, the regulatory test to determine the "toxicity characteristic" of a waste material (USEPA 1999). In the TCLP, a soil sample is crushed after drying to pass a 9.5-mm standard sieve. Depending upon the buffering capacity, the crushed sample is placed either in 0.5-M acetic acid extract or an acetate buffer extract, and the pH is not further adjusted during the 18-hour tumbling period. The liquid-to-solid ratio required in the TCLP is 20:1. Wastes or samples with high alkalinity have a significant effect on the actual pH of the TCLP leaching medium. The regulatory definition of toxicity for lead using this test is 5 mg/L or greater. Copper and zinc are not regulated constituents under the TCLP.

The aggressiveness of leaching at pH 3 is illustrated by comparing the leaching rates at the two pHs from the control soil samples in Table 4. The control samples of all soils leached without pH adjustment had lead concentrations falling between 0.25 and 1.8 mg/L, varying largely with the amount of lead contained in the soil. The amount of lead that was leached into the 50-ml leachate samples varied from about 0.1 percent to 0.4 percent of the original lead that was contained in the contaminated soil samples. These levels of leaching would be expected to continue over many leaching periods or storm events in the field.

In contrast, leaching at pH 3 increased the amount of lead leached from the SAFR soils by 100 to 200 times, the Kodiak soil increasing by nearly 700 times, the amount of lead leached in comparison to the "natural" leachate pH. In fact, large proportions of the lead in the soil samples were removed. Over 60 percent of the original lead content of the Fort Polk and New Orleans soils was found in the 50-ml leachates. The lead concentration in the Kodiak soil without amendment consistently represented about 125 percent of the lead in the original soil. The greater than 100 percent value may be attributable to minute particles of zero-valent lead in these soil samples.

The total lead leached at pH 3 from the spiked WES and kaolin soils varied from 40 to 70 percent of the original lead content. The increase varied largely with the lead content of the soils, the higher lead levels showing the largest effect at the lower pH.

In contrast to the lead-contaminated soils, similar small amounts of lead were lost from the control WES and kaolin soil samples when leached at either pH. Evidently the lead in the natural WES and kaolin soils is in a very stable state with very low solubilities. These soils have probably been leached in the natural states for long periods of time so that most of the less stable forms of lead have been removed or are masked internally in the soil particles or are in geochemical phases that are resistant to leaching at their natural pH and at pH 3.

**Table 4**  
**Comparison of Lead Leaching Rates at pH 3 with Unadjusted Leaching Rates**

Soil, mg/kg lead	Lead in 5-g Sample, mg	Unadjusted Leaching pH			Leaching pH Adjusted to pH 3.0			Ratio of Lead Concentration at pH 3 to Lead Concentration without Unadjusted pH
		Unadjusted Sample pH	Total Lead in Leachate Sample mg	Percent Lead Recovery	Adjusted Sample pH	Total Lead in Leachate Sample mg	Percent Lead Recovery	
Kodiak 10,100	50.5	6.18	0.089	0.18%	3.48	62.7	124.2%	707
Fort Polk 1,289	6.49	5.51	0.034	0.52%	2.82	3.98	61.3%	119
New Orleans 1,012	5.06	7.41	0.017	0.34%	2.52	3.06	60.4%	180
WES 81	0.41	6.26	0.012	2.96%	2.84	0.015	3.6%	1.2
WES 876	4.38	6.54	0.013	0.29%	2.79	1.76	40.1%	139
WES 1,630	8.15	6.03	0.015	0.19%	2.60	4.46	54.7%	293
WES 2,930	14.6	6.41	0.032	0.22%	2.76	4.49	30.6%	140
Kaolin 69	0.34	6.51	0.010	2.94%	2.88	0.004	1.2%	0.4
Kaolin 896	4.48	6.54	0.014	0.30%	2.95	2.41	53.8%	179
Kaolin 1,549	7.74	6.53	0.019	0.24%	2.92	4.65	60.0%	247
Kaolin 2,526	12.6	6.49	0.033	0.26%	2.98	9.05	71.7%	275

## Effects of Chemical Amendments on Lead Leaching Rates

The addition of 1, 3, and 5 percent (weight of amendment/weight of soil) iron and phosphate amendments to the soils followed the procedures outlined in Appendix A, Section 4. A control soil sample without amendment was also carried through the same procedure.

### Effects of amendments on lead leaching rates without pH adjustment

**Colloid and granular, zero-valence iron amendments added on SAFR and spiked WES and kaolin soils without pH adjustment.** The concentrations of lead in leachates from the SAFR and spiked soils treated with granular or colloidal iron are compared in Table 5 for leachates with unadjusted pH. The lead concentrations in leachates from all contaminated and spiked soils were well below the action level of 5 mg/L, and all except the leachates from Kodiak soils were well below 1 mg/L (Table 5). Particulate iron additions affected the lead concentrations in the leachates. The amount of the effect varied somewhat between the different soil types and lead levels. For the Kodiak soil, which had very high lead content (over 10 g/kg), the 5 percent granulated iron reduced the leachate concentration to about two-thirds of the control soil leachates. Colloidal iron had a lesser effect, reducing leachate lead concentrations by 4 to 19 percent.

**Table 5****Lead Concentration in Leachates from Iron-Treated Soils without pH Adjustment**

Soil, mg/kg lead	Granular Iron, mg/L Lead				Colloidal Iron, mg/L Lead			
	Additive Level, % Iron							
	0	1	3	5	0	1	3	5
Fort Polk (1289)	0.67	0.60	0.35	0.25	0.67	0.83	0.66	0.64
New Orleans (1012)	0.34	0.30	0.28	0.28	0.34	0.30	0.29	0.27
Kodiak (10,100)	1.78	1.56	1.36	1.04	1.78	1.56	1.75	1.66
WES (81)	0.220	0.035	0.035	0.035	0.220	0.044	0.027	0.025
WES (876)	0.253	0.287	0.315	0.371	0.253	0.430	0.470	0.497
WES (1,630)	0.304	0.414	0.462	0.512	0.304	0.548	0.564	0.601
WES (2,930)	0.643	0.729	0.749	0.791	0.643	0.812	0.825	0.901
Kaolin (69)	0.252	0.025	0.022	0.049	0.252	0.010	0.025	0.020
Kaolin (896)	0.270	0.094	0.140	0.153	0.270	0.192	0.199	0.247
Kaolin (1,549)	0.376	0.338	0.366	0.366	0.376	0.434	0.462	0.484
Kaolin (2,526)	0.658	0.484	0.528	0.570	0.658	0.732	0.892	0.955

Reductions in leachate lead concentrations were observed for the unspiked, WES, and kaolin soils after treatment with granular and colloidal iron. However, leaching behaviors of the lead-spiked WES and kaolin soils in the presence of the added iron was quite different. The spiked WES soils actually released more lead, up to 2 times more, when either type of iron was added (Table 5). In most cases there were small decreases in leachate lead concentrations after iron addition to the spiked kaolin soils. The two exceptions were the colloidal iron treatment at the higher spiked concentrations in which increases were observed.

**Phosphate amendments added to SAFR soils leached without pH adjustment.** The addition of the phosphate derivatives to the lead-contaminated SAFR soils with no pH adjustment generally reduced the amount of lead in the leachates as seen in Tables 6-8. The levels of lead in the leachates from the control samples again were very low.

**Table 6****Lead Concentrations in Leachates from SAFR Soils with Added Hydroxyapatite and Calcium Phosphate without pH Adjustment**

Soil, mg/kg Lead	Hydroxyapatite Powder, mg/L Lead				Calcium Phosphate, mg/L Lead			
	Additive Level (w/w)							
	0%	1%	3%	5%	0%	1%	3%	5%
Fort Polk (1,289)	0.810	0.035*	0.035*	0.035*	0.794	0.025	0.027	0.036
New Orleans (1,012)	0.340	0.152	0.099	0.035*	0.340	0.112	0.045	0.024
Kodiak (10,100)	0.886	0.035*	0.035*	0.035*	1.78	1.03	0.233	0.117
Camp Keller (2,174)	0.429	0.092	0.398	0.389	0.427	0.364	0.368	0.369

<sup>1</sup> Levels are below detection limits. The number, 0.035 mg/L, is twice the detection limit and included for comparison.

**Table 7****Lead Concentration in Leachates from SAFR Soils with Added Sodium Phosphate and Ammonium Phosphate without pH Adjustment**

Soil, mg/kg Lead	Sodium Phosphate, mg/L Lead				Ammonium Phosphate, mg/L Lead			
	Additive Level (w/w)							
	0%	1%	3%	5%	0%	1%	3%	5%
Fort Polk (1,289)	0.177	0.665	0.618	0.368	0.360	0.367	0.369	0.405
New Orleans (1,012)	0.470	1.04	5.45	7.69	0.420	2.27	1.77	1.81
Kodiak (10,100)	0.510	37.9	91.3	184.3	1.77	8.17	8.65	8.58
Camp Keller (2,174)	nd	nd	nd	nd	nd	nd	nd	nd

Note: nd = not determined.

**Table 8****Lead Concentration in Leachates from SAFR Soils with Added Potassium Phosphate without pH Adjustment**

Soil, mg/kg Lead	Potassium Phosphate, mg/L Lead			
	Additive Level (w/w)			
	0%	1%	3%	5%
Fort Polk (1,289)	0.810	0.270	0.210	0.300
New Orleans (1,012)	0.340	0.224	0.235	0.164
Kodiak (10,100)	1.14	0.210	0.230	0.240
Camp Keller (2,174)	0.474	0.458	0.416	0.456

Hydroxyapatite and calcium phosphate were most effective at reducing lead in the leachates in the Fort Polk, New Orleans, and Kodiak soils. Addition of 5 percent of these amendments lowered the lead concentrations by 90 to 95 percent. Potassium phosphate addition lowered the lead concentrations by 50 to 80 percent.

The Camp Keller soil leachates were unique in that none of the phosphate additions appeared to have a major effect on lead loss during leaching at natural pH. The addition of hydroxyapatite and calcium or potassium phosphates lowered the leachate concentrations in this soil by only 5 to 15 percent of controls in all cases.

Sodium and ammonium phosphate addition increased the amount of lead leached from all of the SAFR soils. These phosphates increased the amount of lead leached in the Fort Polk, New Orleans, and Kodiak soils to from 4 to 360 times the control. Triplicate tests of the sodium-phosphate-amended Kodiak soil were conducted to verify the large increase in leachate concentration. Increasing the quantity of sodium phosphate resulted in color changes in the leachate solutions that ranged from an amber yellow to a dark brown. For these soils, increasing the quantity of sodium phosphate also resulted in a steady rise in the pH of the leachates from about pH 6 or 7 to slightly above pH 11 (Appendix B).

**Phosphate amendments added to spiked WES and kaolin soils leached without pH adjustment.** Leachates from the spiked WES and kaolin soils

without pH adjustment again exhibited low lead concentrations. The results of phosphate additives on leachate lead concentrations from these soils are shown in Tables 9-11. Similar overall leachate lead levels are found for both spiked soil types. Calcium phosphate was the most effective in lowering the lead levels, a 1 percent addition reducing them by 90 to 95 percent of the controls for both the spiked WES and kaolin soils. Hydroxyapatite and potassium phosphate were less effective. They reduced the lead concentrations by 50 to 80 percent depending upon the percent of reagent added.

**Table 9**  
**Lead Concentrations in Leachates from Spiked WES and Kaolinite Soils with Hydroxyapatite Powder and Calcium Phosphate without pH Adjustment**

Soil, mg/kg Lead	Hydroxyapatite Powder, mg/L Lead				Calcium Phosphate, mg/L Lead			
	Additive Level (w/w)							
	0%	1%	3%	5%	0%	1%	3%	5%
WES (81)	0.238	0.050	0.053	0.039	0.238	0.064	0.041	0.017
WES (876)	0.250	0.160	0.137	0.138	0.250	0.030	0.030	0.030
WES (1,630)	0.300	0.143	0.143	0.150	0.300	0.030	0.030	0.030
WES (2,930)	0.660	0.181	0.159	0.151	0.660	0.030	0.030	0.030
Kaolin (69)	0.203	0.016	0.033	0.009	0.203	0.007	0.010	0.014
Kaolin (896)	0.271	0.064	0.044	0.079	0.271	0.070	0.040	0.030
Kaolin (1,549)	0.380	0.059	0.074	0.111	0.380	0.030	0.030	0.030
Kaolin (2,526)	0.660	0.116	0.082	0.107	0.660	0.030	0.030	0.030

**Table 10**  
**Lead Concentration in Leachates from Spiked WES and Kaolinite Soils with Sodium and Ammonium Phosphates at Natural pH**

Soil, mg/kg Lead	Sodium Phosphate, mg/L Lead				Ammonium Phosphate, mg/L Lead			
	Additive Level (w/w)							
	0%	1%	3%	5%	0%	1%	3%	5%
WES (81)	0.238	0.058	0.051	0.060	0.238	0.090	0.057	0.072
WES (876)	0.250	9.17	4.76	0.83	0.250	0.780	0.750	0.750
WES (1,630)	0.300	39.4	26.0	2.32	0.300	0.850	0.790	0.810
WES (2,930)	0.660	84.6	57.6	4.77	0.660	0.890	0.870	0.940
Kaolin (69)	0.203	0.04	0.04	0.05	0.203	0.055	0.073	0.092
Kaolin (896)	0.271	0.82	1.04	0.84	0.271	0.790	0.840	0.860
Kaolin (1,549)	0.380	3.36	1.95	1.15	0.380	0.890	0.870	0.880
Kaolin (2,526)	0.660	5.58	9.66	4.36	0.660	0.910	0.880	0.890

<b>Table 11</b> <b>Lead Concentration in Leachates from Spiked WES and Kaolinite Soils with Potassium Phosphate at Natural pH</b>				
Soil, mg/kg Lead	Potassium Phosphate, mg/L Lead			
	Additive Level (w/w)			
	0%	1%	3%	5%
WES (81)	0.238	0.088	0.087	0.077
WES (876)	0.250	0.120	0.090	0.080
WES (1,630)	0.300	0.180	0.130	0.140
WES (2,930)	0.660	0.300	0.200	0.260
Kaolin (69)	0.203	0.050	0.063	0.079
Kaolin (896)	0.271	0.190	0.170	0.170
Kaolin (1,549)	0.380	0.180	0.160	0.170
Kaolin (2,526)	0.660	0.210	0.180	0.210

Both the sodium and ammonium phosphate additions increased the amount of lead leaching in the spiked WES and kaolin soils by several hundredfold. These increases were similar to those seen in the SAFR soils.

### Effects of amendments on leaching rates with leachant adjusted to pH 3

In these tests, the pH of the leaching sample was adjusted to  $\text{pH } 3 \pm 0.5$  over the 3-day leaching period. Typically, additional acid was required daily to maintain this pH.

**Granulated and colloidal iron amendments added to SAFR soils leached at pH 3.0.** Lead concentration in leachant from the SAFR and the spiked soils before and after treatment with granular and colloidal iron is presented in Table 12. Lead concentrations decreased significantly when the Kodiak soil was treated with granular iron in comparison to colloidal iron at pH 3. Reductions in lead concentration from 1,338 mg/L for the untreated, control soil to 97.7 mg/L for the 5 percent granular iron treatment were achieved whereas a decrease from 1,338 mg/L to only 1,031 mg/L was attained at the 5 percent colloidal iron treatment level. The 5 percent amendment application to Kodiak soil reduced the leachate lead concentration by 94 and 23 percent for granular and colloidal iron, respectively. Application of iron amendments to the Fort Polk and New Orleans soils resulted in marginal reductions in lead concentrations in the leachate samples in comparison to the untreated (0 percent iron) soils. Larger reductions in lead leachant concentrations in the New Orleans soil were observed after amendment with granular iron in contrast to the colloidal iron treatment. Again a 5 percent iron amendment application was the most effective.

In general, neither granular nor colloidal forms of zero-valent iron were effective in reducing the lead loss from most of the soils to below the TCLP action level at pH 3. With the exception of the unspiked WES and kaolin soils,



leachate concentrations from the other soils at all iron addition levels were well above the action level of 5 mg/L.

The results of leaching at pH 3.0 with added granulated iron, which was the more effective form, is shown as percent of the control (no amendment) leachate lead concentration in Figure 13. Except for the spiked WES soils, for which iron addition actually increased the lead leaching rate, the lead concentrations in the other SAFR soils and the spiked kaolin soil were lowered only to roughly 50 percent of control at pH 3. Granulated iron addition had the largest effect on the Kodiak soil, reducing the lead concentration by 94 percent of the control at all iron addition levels at pH 3 in comparison to 84 percent of control at the unadjusted pH. However, even at 6 percent of Kodiak control soil the lead concentration in the leachate was 94 mg/L. With the addition of higher levels of the amendments, further stabilization of the Kodiak soil would be expected.

Table 12								
Lead Concentration in Leachates from Iron-Treated Soils Leached at pH 3.0								
Soil, mg/kg Lead	Granular Iron, mg/L				Colloidal Iron, mg/L			
	Additive Level (w/w)							
	0% Fe	1% Fe	3% Fe	5% Fe	0% Fe	1% Fe	3% Fe	5% Fe
Fort Polk (1,289)	66.5	54.4	39.6	26.6	66.5	47.7	27.3	17.8
New Orleans (1,012)	58.3	52.1	45.8	30.8	58.3	61.3	61.4	50.2
Kodiak (10,100)	1,338	873	395	97.9	1,338	1,313	1,297	1,031
WES (81)	0.29	0.021	0.02	0.016	0.29	0.014	0.023	0.012
WES (876)	35.1	40.2	43.2	25.3	35.1	32.2	32.9	31.5
WES (1,630)	89.1	100	92.4	68.5	89.1	88.0	88.9	90.1
WES (2,930)	179	211	178	150	179	176	179	182
Kaolin (69)	0.08	0.04	0.04	0.07	0.08	0.08	0.06	0.06
Kaolin (896)	48.2	46.0	41.1	27.5	48.2	47.2	47.0	48.4
Kaolin (1,549)	92.9	75.5	81.6	56.6	92.9	139	147	145
Kaolin (2,526)	184	191	170	105	184	188	197	198

**Phosphate amendments added to SAFR soils leached at pH 3.0.** As expected, the lead concentrations in leachates from the test soils at pH 3 generally exceeded those from unadjusted pH leachates by several orders of magnitude (Tables 13-15). At 5 percent addition, all of the phosphate reagents except sodium phosphate lowered the lead concentration of the leachates to below the USEPA action level of 5 mg/L for the Fort Polk, New Orleans, and Camp Keller SAFRs. None of the phosphate amendments was successful at lowering the very high initial lead levels in the Kodiak soil to less than about 10 mg/L. However, potassium and ammonium phosphate reduced the lead leached from the Kodiak soil to less than 1 percent of the control or a 99 percent decrease in lead concentration.

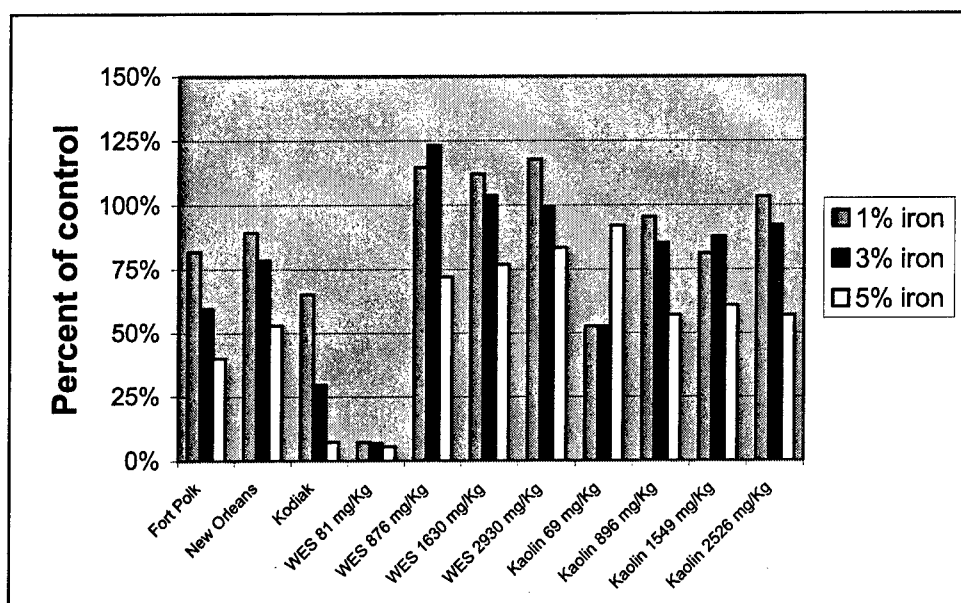


Figure 13. Lead concentration as percent of control leachate concentrations with added granulated iron at pH 3.0

<b>Soil, mg/kg Lead</b>	<b>Hydroxyapatite Powder, mg/L Lead</b>				<b>Calcium Phosphate, mg/L Lead</b>			
	<b>Additive Level (w/w)</b>							
	<b>0%</b>	<b>1%</b>	<b>3%</b>	<b>5%</b>	<b>0%</b>	<b>1%</b>	<b>3%</b>	<b>5%</b>
Fort Polk (1,289)	79.6	6.82	1.25	0.44	79.6	56.2	1.39	0.741
New Orleans (1,012)	61.1	12.1	0.44	0.37	61.1	12.3	0.45	0.320
Kodiak (10,100)	1,255	1,197	955	638	1,255	1,246	880	775
Camp Keller (2,174)	145	16.1	0.915	0.921	141	14.6	1.49	0.466

Some interesting contrasts were observed between the lead leaching behavior at unadjusted pH and at pH adjusted to 3.0. Hydroxyapatite and calcium phosphate at 5 percent addition reduced the lead concentrations for all of the SAFR soils except Kodiak by over 99 percent to less than 1 mg/L. Their addition reduced the lead content of the Kodiak soil leachates to only 50 and 60 percent of the control, or about 640 and 775 mg/L lead, respectively. However, the largest reduction in lead concentration in absolute numbers actually occurred in the Kodiak soil after addition of the phosphate amendments. A comparison of reductions in lead concentrations shows that the average reduction (708 mg/L lead) for the Kodiak soil at 5 percent addition was greater than the average reductions observed for Fort Polk and New Orleans, about 76 and 61 mg/L, respectively.

**Table 14****Lead Concentration in Leachates from SAFR Soils with Potassium and Ammonium Phosphates at pH 3.0**

Soil, mg/kg Lead	Potassium Phosphate, mg/L Lead				Ammonium Phosphate, mg/L Lead			
	Additive Level (w/w)							
	0%	1%	3%	5%	0%	1%	3%	5%
Fort Polk (1,289)	79.6	2.08	1.41	1.66	79.6	3.41	3.21	0.844
New Orleans (1,012)	67.5	7.63	1.76	1.13	60.5	0.442	0.381	0.248
Kodiak (10,100)	1,246	678	58.1	11.4	1,250	820	183	12.2
Camp Keller (2,174)	145	6.95	0.662	0.713	nd	nd	nd	nd

Note: nd = not determined.

**Table 15****Lead Concentration in Leachates from SAFR Soils with Phosphoric Acid and Sodium Phosphate at pH 3.0**

Soil, mg/kg Lead	Phosphoric Acid, mg/L Lead				Sodium Phosphate, mg/L Lead			
	Additive Level (w/w)							
	0%	1%	3%	5%	0%	1%	3%	5%
Fort Polk (1,289)	79.6	15.4	12.5	3.36	79.6	90.1	72.4	12.6
New Orleans (1,012)	60.5	3.70	0.75	0.62	67.5	38.0	8.26	6.15
Kodiak (10,100)	1,250	397	12.1	17.2	1,250	1,120	625	239
Camp Keller (2,174)	nd	nd	nd	nd	nd	nd	nd	nd

Note: nd = not determined

A 5 percent addition of potassium phosphate lowered the control leachate concentrations in the Fort Polk and New Orleans soils to well below the USEPA action level of 5 mg/L. The Kodiak soil was lowered from 1,246 mg/L to 11.4 mg/L, a decrease of 1,235 mg/L or a 99 percent reduction in leachate concentration.

The ammonium phosphate additions at 5 percent reduced the lead levels of the soils by over 98 percent, including the Kodiak soil. Phosphoric acid and sodium phosphate were the least effective but still lowered the lead concentrations in all SAFR soils by more than 80 to 95 percent. These two amendments were more effective than hydroxyapatite and calcium phosphate with the Kodiak soil, lowering the lead concentration from 1,250 mg/L to 17 and 238 mg/L, respectively.

**Phosphate amendments added to spiked WES and Kaolin soils leached at pH 3.0.** The two lead-spiked soils had similar results when exposed to the different phosphate reagents as seen in Tables 16-18. The spiked soils produced approximately 100 to 300 times higher lead concentrations in leachates at pH 3. In contrast, the unspiked WES and kaolin soils lost similar amounts of lead in

both pH regimes. In general, the amount of lead leached from each of the spiked soils increased with the level of lead in the soil and decreased with an increase in the added phosphate reagent.

**Table 16**  
**Lead Concentration in Leachates from Spiked WES and Kaolin**  
**Soils with Hydroxyapatite and Calcium Phosphate Leached at**  
**pH 3.0**

Soil, mg/kg Lead	Hydroxyapatite Powder, mg/L Lead				Calcium Phosphate, mg/L Lead			
	Additive Level (w/w)							
	0%	1%	3%	5%	0%	1%	3%	5%
WES (81)	0.29	0.010	0.073	0.019	0.29	0.043	0.017	0.022
WES (876)	35.1	0.81	0.43	0.30	35.1	0.84	0.21	0.06
WES (1,630)	89.1	7.99	1.48	1.01	89.1	14.7	0.89	0.35
WES (2,930)	89.8	28.4	4.28	1.43	89.8	55.8	6.12	1.24
Kaolin (69)	0.08	0.118	0.098	0.139	0.08	0.059	0.101	0.124
Kaolin (896)	48.2	5.20	0.35	0.27	48.2	3.71	0.36	0.22
Kaolin (1,549)	92.9	6.64	1.80	0.73	92.9	18.3	0.52	0.09
Kaolin (2,526)	181	36.1	1.88	1.04	181	51.1	2.71	0.38

**Table 17**  
**Lead Concentration in Leachates from Spiked WES and Kaolin**  
**Soils with Potassium and Ammonium Phosphates Leached at**  
**pH 3.0**

Soll, mg/kg Lead	Potassium Phosphate, mg/L Lead				Ammonium Phosphate, mg/L Lead			
	Additive Level (w/w)							
	0%	1%	3%	5%	0%	1%	3%	5%
WES (81)	0.29	0.065	0.091	0.116	0.29	0.043	0.032	0.044
WES (876)	35.1	6.49	0.97	0.65	35.1	4.61	1.39	1.15
WES (1,630)	89.1	32.7	4.68	2.26	89.1	23.1	3.76	2.25
WES (2,930)	89.8	73.7	10.8	4.57	89.8	51.22	6.86	3.48
Kaolin (69)	0.08	0.061	0.048	0.072	0.08	0.025	0.025	0.036
Kaolin (896)	48.2	7.80	0.81	0.53	48.2	4.76	1.10	0.96
Kaolin (1,549)	92.9	36.8	3.04	1.41	92.9	23.2	2.49	1.58
Kaolin (2,526)	181	77.4	6.23	2.23	181	46.6	4.11	2.21

The addition of 5 percent weight per weight (w/w) of all of the phosphate reagents except phosphoric acid reduced the concentration of lead in leachates to below 5 mg/L. At 5 percent addition, the leachates from hydroxyapatite and calcium phosphate soil samples were near or below 1 mg/L. Addition of 3 percent hydroxyapatite and calcium, potassium, and ammonium phosphates also lowered the leachate concentrations to this level for all spiked soils except the WES soil with the highest spike.

At pH 3, the sodium phosphate amendment reduced the lead concentrations in leachates at all addition rates, in contrast to their action without pH adjustment

where the addition of sodium phosphate greatly increased the lead concentrations. This difference is likely due to formation of different lead species at pH 3 and an increase in phosphate availability at the same pH.

**Table 18**  
**Lead Concentration in Leachates from Spiked WES and Kaolin**  
**Soils with Phosphoric Acid and Sodium Phosphate Leached at**  
**pH 3.0**

Soil, mg/kg Lead	Phosphoric Acid, mg/L Lead				Sodium Phosphate, mg/L Lead			
	Amendment Level (w/w)							
	0%	1%	3%	5%	0%	1%	3%	5%
WES (81)	0.29	0.016	0.048	0.083	0.29	0.059	0.043	0.045
WES (876)	35.1	0.75	1.15	1.36	35.1	9.17	4.76	0.83
WES (1,630)	89.1	3.79	3.73	3.55	89.1	39.4	26.0	2.32
WES (2,930)	89.8	8.44	9.24	7.75	89.8	84.6	57.6	4.77
Kaolin (69)	0.08	0.015	0.058	0.281	0.08	0.047	0.069	0.095
Kaolin (896)	48.2	0.36	2.52	13.4	48.2	17.7	4.73	0.87
Kaolin (1,549)	92.9	1.95	11.8	31.0	92.9	55.1	25.5	2.98
Kaolin (2,526)	181	3.48	27.0	63.1	181	101	52.7	3.85

**Effectiveness of hydroxyapatite and calcium phosphate in stabilizing lead in all soils.** Hydroxyapatite powder and calcium phosphate produced leachates with the lowest lead concentrations at the lowest amendment levels. These results are illustrated in Figure 14 and Figure 15 for hydroxyapatite, and Figure 16 and Figure 17 for calcium phosphate. The scales in Figures 15 and 17 are expanded to emphasize the lead concentrations below 5 mg/L. Addition of 5 percent of either amendment brought the lead levels near or below 1 mg/L.

#### **Relationship between the ratio of the concentrations of additive to lead in the soil, to the amount of reduction in lead concentration in the soil leachates**

Figures 18-20 compare the ratio of the levels of calcium phosphate, hydroxyapatite, and potassium phosphate to lead in the original soil sample with the relative effectiveness of the additives in reducing the amount of lead in the pH 3 leachates. The effectiveness is measured by the ratio of the amount of lead in treated leachates to the amount of lead in the control leachates. The least-squares regression points are included for comparison.

There is a good positive correlation between the amount of additive per unit lead and the effectiveness of the additive treatment ( $r^2 = 0.81$  for hydroxyapatite and 0.66 for calcium phosphate and 0.45 for potassium phosphate). This correlation includes all of the soils in the study, from the Kodiak soil with

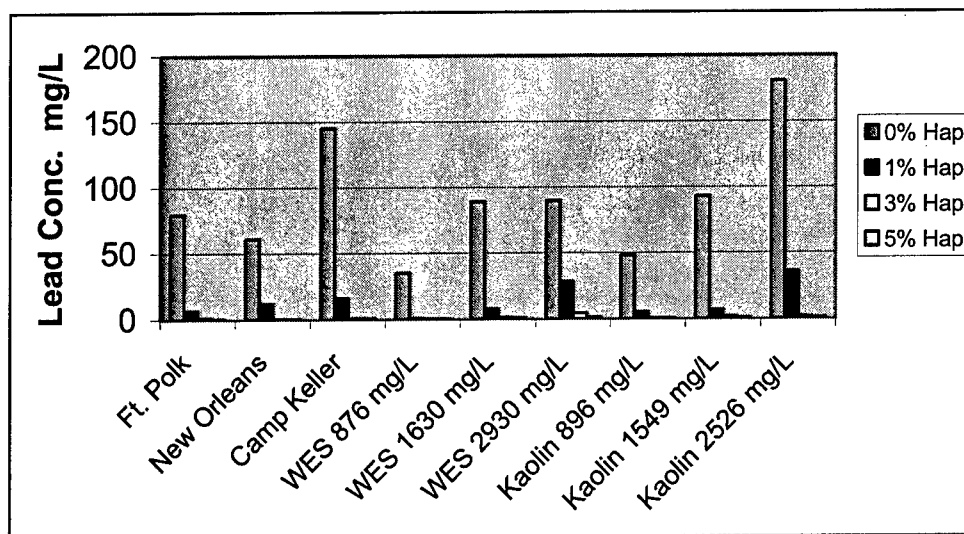


Figure 14. Lead concentration in leachates from soils treated with hydroxyapatite (Hap)

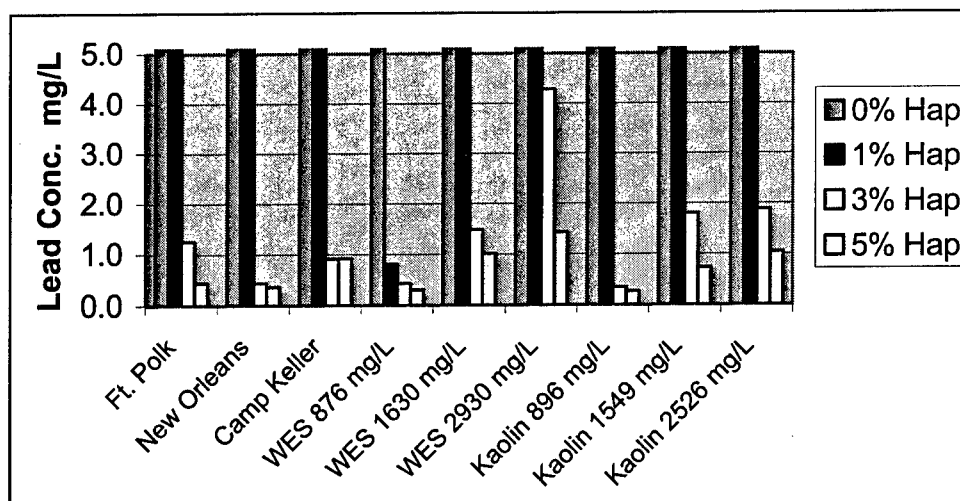


Figure 15. Lead concentration in leachates from soils treated with hydroxyapatite, scale expanded

10 g/kg lead to the spiked soils with less than 1 g/kg lead to near 3 g/kg lead in the soil. The least-squares regression equations are as follows:

- a. For calcium phosphate:

$$\log(x) = -0.33 \log(y) + 0.74; r^2 = 0.66 \quad (1)$$

- b. For hydroxyapatite:

$$\log(x) = -0.55 \log(y) + 0.31; r^2 = 0.81 \quad (2)$$

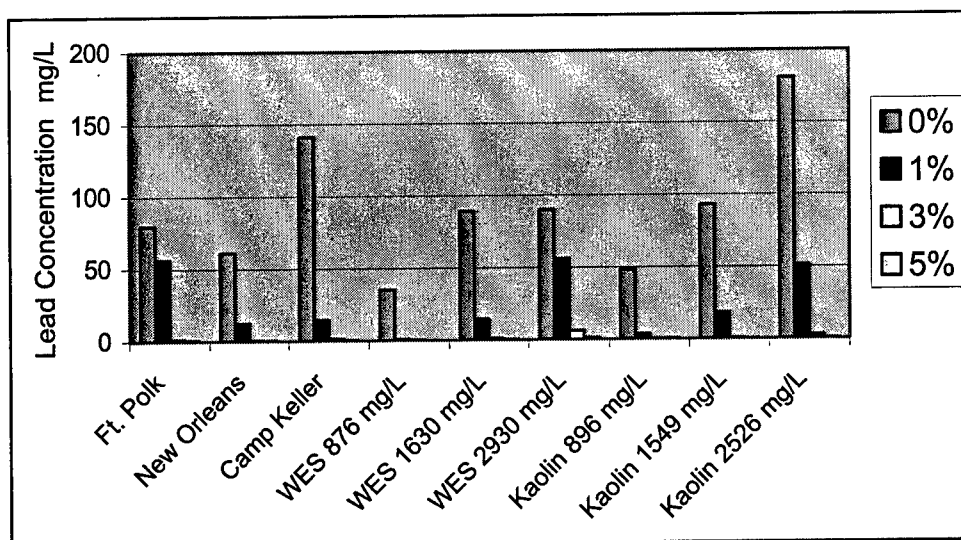


Figure 16. Lead concentration in leachates from soils treated with added calcium phosphate

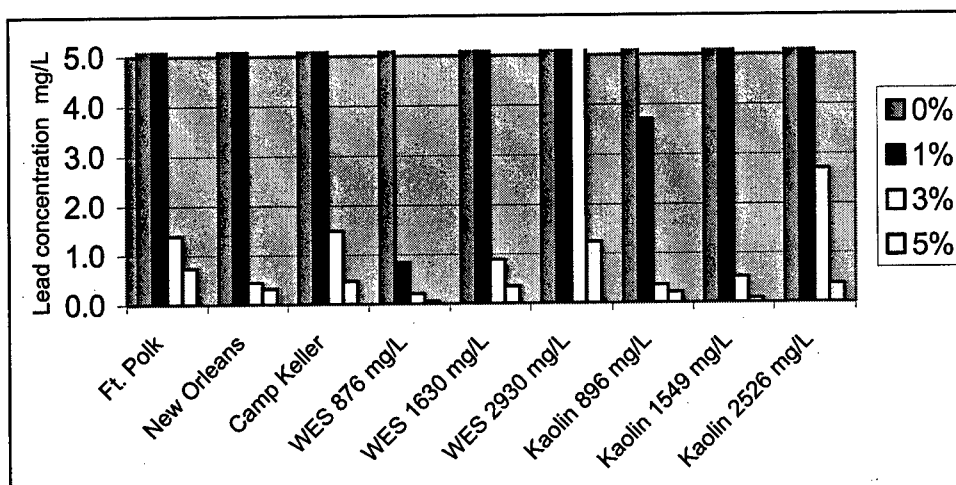


Figure 17. Lead concentration in leachates from soils treated with calcium phosphate, expanded scale

c. For potassium phosphate:

$$\log(x) = -0.46 \log(y) + 0.50; r^2 = 0.45 \quad (3)$$

The effect of increased additive levels on lead stabilization is a nonlinear function and apparently asymptotic to zero leachate lead concentrations. As the concentration of additive relative to lead content in the soil increases, its effectiveness decreases and larger amounts of additive are required to achieve the same stabilization effectiveness. This is seen across all lead contamination levels and soil types. Soils with low lead levels require less additive per unit of lead than soils like the Kodiak soil with higher lead contents. However, even soils with very high lead content should be candidates for stabilization by phosphate addition.

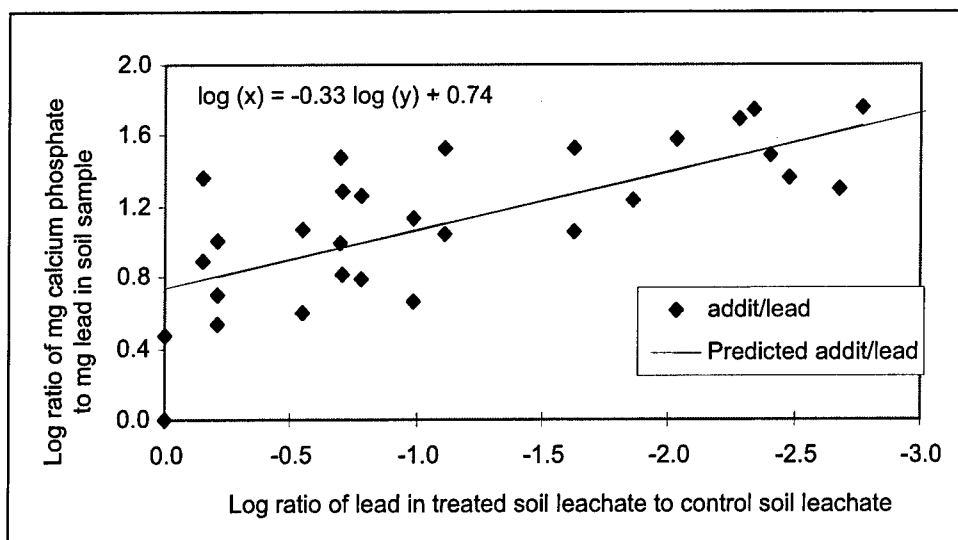


Figure 18. Plot of the log of the ratio of calcium phosphate to lead in soil (Addit/lead) versus the log of the reduction in lead concentration in treated soil leachates at pH 3

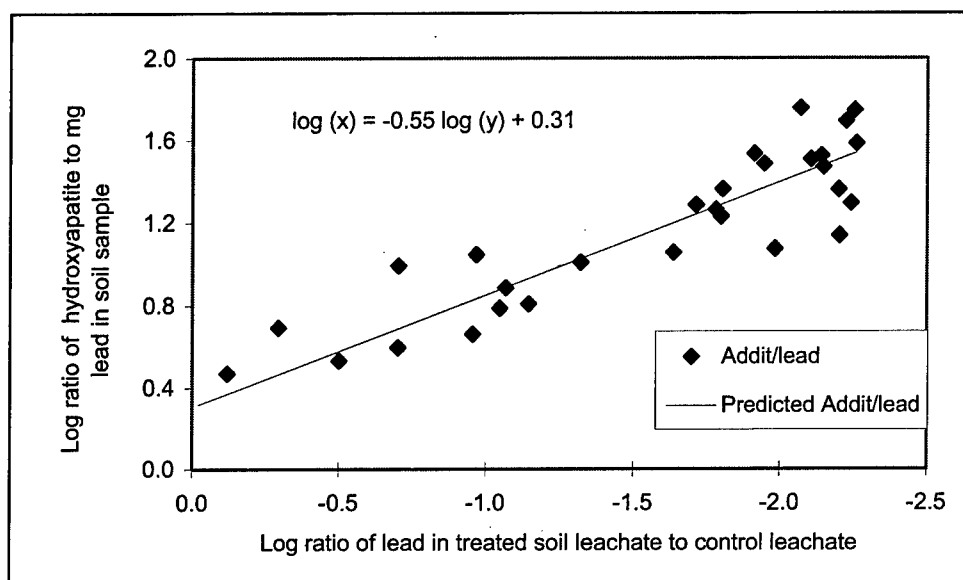


Figure 19. Plot of the log of the ratio of hydroxyapatite to lead in soil (Addit/lead) versus the log of the reduction in lead concentration in the treated soil leachates at pH 3

### Leaching of Kodiak soil

The results with the Kodiak soil were unique due to its very high lead content (over 10 g/kg) even after removing the whole and fragmented bullets. The Kodiak soil was composed of mostly a fine fly ash and sandy material (Bricka et al. 1999). A summary of the results of all phosphate amendments and their relative effectiveness for the Kodiak soil is shown in Table 19.



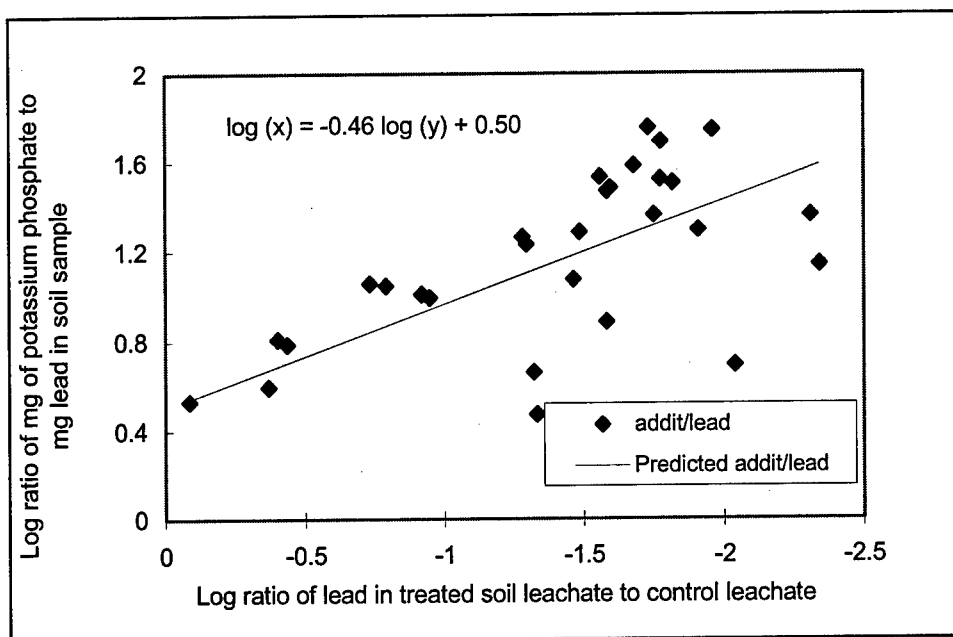


Figure 20. Plot of the log of the ratio of potassium phosphate to lead in soil (Addit/lead) versus the log of the reduction in lead concentration in the treated soil leachates at pH 3

Table 19							
Lead Concentration in pH 3 Leachates from Kodiak Soil with Phosphate Amendments and as Percent of Control							
Soil Amendment to Kodiak Soils	Lead Concentration, mg/L				Amendment Effectiveness as Percent Reduction in Leachate lead Concentrations		
	Amendment Level, percent						
	0	1	3	5	1	3	5
Hydroxyapatite	1255	1197	955	639	5	24	49
Calcium phosphate	1255	1246	880	775	1	30	38
Sodium phosphate	1246	1120	625	239	10	50	81
Potassium phosphate	1246	678	58.1	11.4	46	95	99
Ammonium phosphate	1250	820	183	12.2	34	85	99
Phosphoric acid	1250	397	12.1	17.2	68	99	99

Comparing the level of amendment added to the level of lead in the soils, the Kodiak soil had 5 to 10 times as much lead per added reagent as the other soils. Although none of the amendments reduced the lead level to below 5 mg/L in the Kodiak soil, the three more soluble phosphate reagents at the levels used did reduce the lead concentration in pH 3 leachates to less than or near 1 percent of the untreated control levels, i.e., were over 99 percent effective in reducing the lead concentration in the leachates. The addition of greater quantities of amendment (> 5 percent) would be expected to reduce lead concentrations to levels similar to the other soils.

### **Overall effectiveness of phosphate amendments**

Although all were effective in reducing lead losses, the less soluble forms, hydroxyapatite and calcium phosphate, typically produced the lowest lead concentrations. The more soluble forms were also effective but to a lesser degree. Sodium phosphate acted as a highly basic leachant, producing leachates high in lead content in a manner similar to leaching at the lower, acidic pH. Consequently, sodium phosphate was the least effective amendment at the unadjusted, natural soil pH. Its effectiveness increased after leaching and pH adjustment to 3.0. A similar trend was observed for ammonium phosphate.

The treatment of lead-contaminated soils with phosphate reagents has been shown to be a viable method of reducing lead solubility even when leached at pH 3. The treatment of soils with the highly soluble forms of phosphate such as sodium, potassium, or ammonium phosphates may increase the risk of offsite phosphate migration resulting in eutrophication of surrounding surface waters (Ma et al. 1993). The approach of using phosphate sources that have lower solubilities, but are still effective, such as apatite may alleviate this problem. These calcium phosphates are prevalent as accessory minerals in igneous rocks and as low-temperature precipitates in soils and sedimentary environments (Traina and Laperche 1999).

## 4 Summary and Conclusions

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Forms of the orthophosphate ion are sparingly soluble solids when reacted with several toxic metals, including lead, zinc and cadmium. The lead phosphates are some of the least soluble solids known. At the standard state, lead phosphates are at least 44 orders of magnitude less soluble than lead sulfide (galena), lead sulfate (anglesite), lead carbonate (cerussite), lead oxide (litharge), and lead chromate (crocoite) (Traina and Laperche 1999). In oxidized, noncalcareous environments, pyromorphites should form at the expense of adsorbed or other forms of lead solids if sufficient phosphate is present.

This research was undertaken to develop a testing procedure for determining the capacity of zero-valent iron and selected phosphate reagents to immobilize lead in contaminated soils from small arms firing ranges (SAFRs). Four soils sampled from actual SAFRs were tested along with two well-defined soils that were spiked with three levels of lead. The contaminated and spiked soils were leach tested with three levels of the additives, both without pH adjustment and with continuous adjustment to  $\text{pH } 3.0 \pm 0.5$ . The pH 3 leach provided a very aggressive leaching test. Soils were leached for 3 days, filtered, and the leachates analyzed for lead.

SAFR soils are open dynamic systems that are mixtures of various meta-stable solids. Multiple chemical forms of most metals are usually present at any given time. Which forms are present is controlled by the reaction dynamics and the total quantity of the most reactive forms of the metals that are present. An ideal treatment technique would facilitate the complete conversion of the toxic elements (lead in the current study) to their most geochemically stable form. The chemical reactivity and bioavailability of toxic elements can be decreased significantly by elimination of the most reactive forms.

Testing lead leaching rates at the natural, unadjusted pH of the soil and at pH 3 provided essential data for the study. Only very low concentrations of lead were leached from the soils at the natural pH of the soils, which are typical of the leaching conditions cited in most research literature (Chen et al. 1997; Ma et al. 1993, 1995). However, results at "natural" pH values may not be indicative of the long-term environmental impact of lead leaching and migration at SAFRs because these processes may occur over hundreds of years.

Accelerated leaching tests at pH 3 provided a method of estimating the maximum concentrations of leachable lead for each soil under the test conditions. A correlation between these results and maximum leachate lead concentrations at

SAFRs after hundreds of years has not been established. Nonetheless, the data resulting from aggressive soil leaching and chemical treatment at low pH provided information on the ability of chemical amendments to impact lead bioavailability and leaching rates.

A second consideration addressed in this study was the amount of amendment required for adequate reduction in lead solubility. Very low levels of amendment were used in this study (1, 3, and 5 percent w/w) compared with those used in many other studies. For instance, Ma et al. (1993) added from 8 to 33 percent (w/w) hydroxyapatite to soil at pH 4.3 in their study. Laperche et al. (1997) used an approximate 1:1 ratio of soil to hydroxyapatite and Chen et al. (1997) studied the effects of variable pH values on solutions having 1.2 g of hydroxyapatite in 35 ml containing 0.87 to 0.54 g of lead.

Granular, zero-valent iron and phosphate amendments were found to be effective in stabilizing lead in the soils at low application rates. At comparable application rates, phosphate amendments were much more effective than the granulated iron treatment. The highest treatment efficiency for the granular iron amendment was approximately 40 percent of the untreated, control-leaching rate, in comparison to less than 1 percent for most phosphates amendments.

Powdered hydroxyapatite, and calcium, potassium, and ammonium phosphates were the most effective phosphate amendments for reducing lead loss in the SAFR and lead-spiked WES and kaolin soils, both at the natural pH of the soil and at pH 3. On average, a 3 percent (w/w) application was sufficient in reducing leachable lead to near 1 percent of the control. In contrast, sodium phosphate and colloidal iron were ineffective as amendments even at the "natural" pH of the soils.

Leaching sodium phosphate and to a lesser extent ammonium phosphate amended soils at the natural pH resulted in increased instead of decreased leachate lead concentrations. Compared to leachates from control soil samples, amendment additions increased both the pH and lead concentrations. However, in the accelerated leaching tests at pH 3, sodium and ammonium phosphate amended soils had rates of leaching similar to those of the other phosphate amended soils.

The effectiveness of the calcium phosphate and hydroxyapatite additives was found to be nonlinearly related to the ratio of the additive to the lead concentration in the soil. The effectiveness of the additives decreased as the ratio of additive to lead increased. SAFR soils with higher lead content would require higher levels of phosphate amendment as predicted from studies using cleaner, lower-lead-content soils.

Specific recommendations from the study are as follows:

- a. A 3 percent application of hydroxyapatite or calcium or potassium phosphate is recommended as a remediation strategy for reducing leaching and bioavailability of lead in contaminated SAFR soils with low to moderate levels of lead. SAFR soils with higher lead contamination may require higher additive levels.

- b.* Large-scale laboratory tests and detailed cost analyses of the phosphate chemicals are necessary before recommendations can be made concerning the selection of a specific amendment and an application technique.
- c.* Granular iron may be effective for treatment of soils with similar physical and chemical characteristics to the Kodiak soil but in general are not as effective as phosphate materials.
- d.* Sodium and ammonium phosphate amendments are not recommended for use for lead-contaminated SAFR soils.

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# Appendix A

## Experimental Protocols

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A detailed listing of techniques and procedures for the tests developed in this study is presented in this appendix. These protocols should be of value to researchers who may be using these or similar techniques in their work. Mention of specific trade or company names is for example only and is not meant as endorsements of the equipment or supplies.

### Section 1: SAFR, WES and Kaolinite Soil Preparation

#### Scope

This laboratory protocol describes the procedures used for preparing soils for this study. Section 1 describes the preparation and pretesting procedures for small arms firing ranges (SAFR), WES,<sup>1</sup> and kaolin soils. Section 2 covers preparation of lead-spiked WES and kaolin soils.

#### Summary of procedures

The SAFR soils (Fort Polk, New Orleans, Kodiak, Camp Keller) and WES and kaolin soils are pretested for moisture content, pH properties, and oxidation-reduction potential (ORP). Quantities of the soils required for laboratory testing are calculated, weighed, and dried in an oven. The dried soil samples are ground into a fine powder, sieved, and stored in plastic bottles. The quantity of dilute nitric acid needed to adjust the soils to pH 3 is determined on a subsample of each soil.

#### Materials

- a. 1,000-ml plastic bottles
- b. 60-ml plastic bottles

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<sup>1</sup> Previously characterized by Bricka et al. (1999) at the U.S. Army Engineer Research and Development Center, Vicksburg, MS.

- c. Adhesive labels
- d. Plastic weighing boats (large)
- e. Stainless steel drying pans
- f. Metal spatula
- g. pH paper (range 2-5)
- h. Distilled deionized (DDI) wash bottle
- i. Kimwipes®
- j. Syringes, sterile (60 ml)
- k. Syringe filters (0.45 µm)

### Reagents

- a. DDI water
- b. Ultrex concentrated nitric acid

### Equipment

- a. Rotar tap sieve apparatus (W.S. Tyler Model RX 29)
- b. Pulverisette 7 soil grinder (Fritsch)
- c. Analytical balances (Mettler AE 240)
- d. Vacuum filtering apparatus
- e. ORP/pH meter (Beckman φ 45)
- f. Laboratory rotary tumbler
- g. Microwave digester (O.I. Analytical BC# F4624)

### Soil pretesting

- a. Sieve each soil collected from the sites over a ¼-inch mesh sieve.
- b. Determine pH and ORP by procedures outlined in “Standard Methods for the Examination of Water and Wastewater” (American Public Health Association 1998) and SW-846 (U.S. Environmental Protection Agency (USEPA) 1999) Method 9045, respectively.<sup>1</sup>

### Sample preparation

- a. Weigh 2000 grams each of SAFR, WES, and kaolin soil into separate stainless steel drying pans and dry at 110 °C for a minimum of 24 hours.
- b. Grind the soils to a fine powder in the soil grinder.

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<sup>1</sup> References cited in this appendix are included in the References section at the end of the main text.

- c. Sieve soils over a 120-mesh sieve and place them in labeled plastic bottles.
- d. Digest the soils according to EPA SW-846 Method 3051 and analyze each for lead (Pb) by EPA SW-846 Method 7420, Flame Atomic Absorption Spectroscopy (AAS).

### **pH adjustment pretesting**

- a. For each soil in Step c of "Sample preparation," label three 60-ml plastic bottles and three 50-ml centrifuge tubes with the name of soil and pH 3.
- b. Weigh three 5-gram samples of these soils in Step c into the labeled plastic bottles.
- c. Add about 25 ml DDI water to each soil and mix.
- d. Add 5 ml of 0.2-M Ultrex nitric acid to each bottle. Vigorously shake the bottles, then check the pH with pH paper.
- e. Continue with the preceding step until the pH is lowered to between  $3.0 \pm 0.5$ . Record each aliquot of liquid (acid and water) added to the bottle.
- f. Place the 60-ml bottles on the tumbler for 10 minutes.
- g. On a pH/ORP meter, measure the initial pH and ORP by placing the electrodes in the liquid layer of the soil mixture. Record results.
- h. Place the 60-ml bottles back on tumbler. Stop the tumbler after 4 hours and re-check pH with pH paper. If the pH increases above 3.0, add additional acid. After adjusting to the desired pH add DDI water to a volume of 50 ml. Continue tumbling the samples for a total of  $24 \pm 2$  hours.
- i. Transfer the samples in the 60-ml bottles to the prelabeled 50-ml centrifuge tubes prepared in Step a of the pretesting and centrifuge the samples at room temperature for 20 minutes at 6000 rpm.
- j. Attach a 0.45- $\mu$ m syringe filter to a 60-ml plastic syringe and place the syringe on the vacuum filtering apparatus. Place labeled bottles inside the filtering apparatus to collect the filtrate. Pour the centrifuged aqueous phase into the syringe, turn on the vacuum, and filter the samples.
- k. Measure the final pH and ORP of the liquid samples on the meter and record results.

## **Section 2: Preparation of Lead-Spiked Soils**

### **Scope**

This laboratory protocol describes the procedures for spiking WES and kaolinite soils with various concentrations of a lead-based compound. Quantitation of lead in the spiked soils is by AAS.

## Summary of procedures

Quantities of WES and kaolin soils are spiked with various concentrations of lead (II) nitrate then carried through a washing procedure. The aqueous and solid phases are separated. After the spiked soils are dried, ground to a fine powder, and sieved, they are stored in plastic bottles for later use. The soils are digested and analyzed for lead by AAS.

## Materials and reagents

- a. Plastic bottles (1,000 ml, 60 ml).
- b. Volumetric flasks (1,000 and 2,000 ml).
- c. Refer to Section 1 for other materials.
- d.  $\text{Pb}(\text{NO}_3)_2$ , lead (II) nitrate.
- e. Refer to Section 1 for other reagents.

## Equipment

- a. Centrifuge (IEC PR-7000 and IEC B 22M).
- b. Desiccator and desiccant.
- c. Refer to Section 1 for other equipment.

## Soil spiking procedure

- a. Prepare a 100,000 mg/L Lead Stock Solution as follows: Dry about 200 g of lead (II) nitrate for 1 hour in an oven set at 110 °C. Cool and store in a desiccator. Weigh 160 g of the  $\text{Pb}(\text{NO}_3)_2$  into a large weighing boat. Volumetrically transfer the  $\text{Pb}(\text{NO}_3)_2$  into a 1-L volumetric flask using DDI water and dilute to volume.
- b. Prepare 2,000, 1,000, and 500 mg/L Lead Spike Solutions by pipeting 40, 20, and 10 ml of the 100,000-mg/L Lead Stock Solution into separate 2-L volumetric flasks. Dilute each flask to volume with DDI water.
- c. Weigh out four separate 300-g samples of WES and kaolinite soils into 1,000-ml plastic bottles.
- d. Add 500 ml of the 2,000-ppm Lead Spike Solution to each of the bottles.
- e. Prepare the 1,000-ppm and 500-ppm spiked soils by repeating *c* and *d* using the 1,000-ppm and 500-ppm Lead Spike Solutions.
- f. Mix the spiked soils on the rotary tumbler for  $72 \pm 2$  hours.
- g. Centrifuge the spiked samples at 3,000 rpm for 1 hour.
- h. Decant each liquid, weigh it, and store it in a clean plastic bottle.
- i. Add about 500 ml DDI water to the solid portion of the centrifuged samples.

- j.* Mix the solid/aqueous phases by stirring with a spatula, then place the samples on the rotary tumbler for 30 minutes.
- k.* Centrifuge the samples at 3,000 rpm for 1 hour.
- l.* Pour off the liquid phase, weigh it, and store it for later analysis by AAS.
- m.* Continue procedures *i* through *l* for a minimum of three soil washings.
- n.* Dry the spiked soils in an oven set at 110 °C for  $24 \pm 2$  hours.
- o.* Grind the soil and then sieve the soils over a 120-mesh sieve and store them in labeled plastic bottles.
- p.* Digest the soils according to EPA SW-846 Method 3051 and analyze each for lead (Pb) by EPA SW-846 Method 7420 AAS.

## Section 3: Soil Leaching Protocol

### Scope

This procedure outlines the Soil Leaching Protocol (SLP) that was used in establishing peak lead concentration versus time data for soils leached with DDI water and with acidified water.

### Summary of procedures

The SAFR soils (Fort Polk, New Orleans, Kodiak, Camp Keller) and WES and kaolin soils prepared as described in this appendix were carried through a SLP. The soils were leached with DDI water and with acidified water at pH 3. The leaching procedure was conducted at the natural pH of the soil and at pH  $3 \pm 0.5$  for periods of 0.8, 1, 3, 5, 7, and 10 days. The leachate samples were filtered and analyzed for lead.

### Materials and reagents

- a.* Plastic bottles (60 ml, 1,000 ml)
- b.* Adhesive labels
- c.* Plastic weighing boats (large)
- d.* Metal spatula
- e.* pH paper (range 2-5)
- f.* DDI wash bottle
- g.* Kimwipes
- h.* Syringes, sterile (60 ml)
- i.* Syringe filters (0.45  $\mu$ m)
- j.* DDI water

- k.* Ultrex concentrated nitric acid
- l.* Scintillation vials (20 mL)

### Equipment

- a.* Analytical balance (Mettler AE 240)
- b.* Vacuum filtering apparatus
- c.* ORP/pH meter (Beckman  $\phi$  45)
- d.* Laboratory rotary tumbler
- e.* Centrifuge (IEC PR-7000 and IEC B-22M)
- f.* AAS
- g.* Inductively coupled plasma-mass spectrophotometer (ICP-MS)

### Leaching protocol

- a.* Label 60-ml plastic bottles and 50-ml centrifuge tubes with the name of each soil prepared in Section 1. Prepare bottles for triplicate runs for each soil and for testing at both pH 3 and at the natural pH of the soil.
- b.* Weigh 5-gram samples of each of the soils into the plastic bottles. Weigh a set of soil samples (in triplicates) for leaching at the natural soil pH and at pH 3 for periods of 0.8, 1, 3, 5, 7, and 10 days.
- c.* Add 50 ml of DDI water to the sample set designated for testing at the natural soil pH.
- d.* Add 25 ml DDI water and 5 ml of 0.2-M nitric acid to the set of samples for leaching at pH 3.
- e.* Vigorously shake the bottles containing the pH 3 samples, then check the pH of the samples with pH paper.
- f.* Continue adding acid in 1- to 2-ml increments, shaking the samples and checking the samples with pH paper until the pH is lowered to between  $3.0 \pm 0.5$ . Record each aliquot of acid added to the bottle.
- g.* Place the samples from *c* and *f* on the tumbler for 10 minutes.
- h.* Measure the initial pH and ORP of the samples on a pH/ORP meter by placing the electrodes in the liquid layer of the soil mixture. Record results.
- i.* Place the samples back on the tumbler. Stop the tumbler periodically and re-check the pH 3 samples with pH paper. If the pH increases above 3.0, add additional acid in 1-ml increments. After the pH stabilizes add DDI water to a volume of 50 ml and continue tumbling the samples for the specified times.
- j.* Transfer the samples to the prelabeled 50-ml centrifuge tubes and centrifuge the samples at room temperature for 20 minutes at 6,000 rpm.

- k.* Place 60-ml plastic syringes on the vacuum filtering apparatus and attach 0.45- $\mu$ m syringe filters. Place labeled bottles inside the filtering apparatus to collect the filtrate. Pour the aqueous phases of the centrifuged samples into the syringes, turn on the vacuum, and filter the samples.
- l.* Pour a 10-ml aliquot of each sample into a 20-ml scintillation vial and measure the final pH and ORP of the samples with the meter. Record results.
- m.* Add concentrated nitric acid, dropwise, to the remaining filtrate to adjust the pH of the samples to  $< 2$  and store the samples at 4 °C.
- n.* Analyze the liquid filtered samples having a lead concentration at or above 1 mg/L on the Perkin Elmer 5100 PC Flame AAS following the USEPA SW-846 Method 7420. Analyze the samples below 1 mg/L lead according to USEPA SW-846 Method 6010 (Inductively Coupled Argon Plasma (ICAP)) or by USEPA SW-846 Method 6020 (ICP-MS).

## Section 4: Application of Soil Amendments

### Scope

Application of various chemicals to soils to screen and identify materials that inhibit lead mobility is described in this laboratory protocol. Samples generated from the study are analyzed according to their lead content by AAS, ICAP, or ICP-MS.

### Summary of procedures

Specific chemicals are added to the SAFR soils and lead-spiked WES and kaolin soils that were prepared as described in this appendix. The soils are carried through a chemical treatment protocol (CTP). The aqueous and solid components of the soils are separated. The liquid leachate component is analyzed for lead (Pb).

### Materials

- a.* 60-ml plastic bottles
- b.* Adhesive labels
- c.* Plastic weighing boats (large)
- d.* Metal spatula (scoop)
- e.* 60-ml centrifuge tubes
- f.* DDI wash bottle
- g.* Kimwipes

## Reagents

- a. DDI water
- b. Granular iron
- c. Colloidal iron
- d. Hydroxyapatite powder (Bio-Rad)
- e. Calcium phosphate, sodium phosphate, potassium phosphate, ammonium phosphate

## Equipment

- a. Analytical balances (Mettler AE 240)
- b. Centrifuge (IEC PR-7000 and IEC B-22M)
- c. Vacuum filtering apparatus
- d. ORP and pH meter (Beckman  $\phi$  45)
- e. Laboratory rotary tumbler
- f. AAS
- g. ICP-MS
- h. ICAP

## Chemical treatment at natural soil pH

- a. For each iron and phosphate chemical listed in Section 4 at concentrations of 1, 3, and 5 percent, label 60-ml plastic bottles for each soil (SAFRs, WES, kaolin, lead-spiked WES, lead-spiked kaolin). Prepare triplicate samples for each soil, chemical, and chemical concentration. Consult Table A1 as an example.
- b. Weigh  $5 \pm 0.2$  g soil into each labeled 60-ml plastic bottle.
- c. Weigh 1, 3, and 5 percent w/w (chemical weight/soil weight) of the chemical into three weighing boats, then transfer the weighed chemical into the 60-ml plastic bottles.
- d. Add 50 ml DDI water to the bottles, cap the bottles, and then place them on the rotary tumbler for 20 minutes.
- e. Measure the initial pH and ORP of the samples with the pH/ORP meter by placing the electrodes in the liquid layer of the soil mixture. Record results.
- f. Place the samples on the rotary tumbler for  $72 \pm 2$  hours.
- g. Transfer the samples to the prelabeled 50-ml centrifuge tubes and centrifuge the samples at room temperature for 30 minutes at 6,000 rpm.
- h. Place 60-ml plastic syringes on the vacuum filtering apparatus and attach 0.45- $\mu$ m syringe filters. Place labeled bottles inside the filtering



apparatus to collect the filtrate. Pour the aqueous phases into the syringes, turn on the vacuum, and filter the samples.

- i.* Pour about 10 ml of each filtrate into a 20-ml plastic scintillation vial and remeasure the pH and ORP of the sample on the meter. Record results.
- j.* To the remaining filtrate add concentrated nitric acid, dropwise, to preserve the samples at pH <2. Store the samples at 4 °C.
- k.* Analyze the liquid filtered samples for lead concentration by AAS, ICAP, or ICP-MS as appropriate.
- l.* Repeat steps *b* through *k* for each soil (SAFRs, WES, kaolin, lead-spiked WES, and lead-spiked kaolin) listed in this appendix, and for each chemical reagent listed in Section 4 at each treatment concentration (1, 3, and 5 percent w/w).

**Table A1**  
**Example of Sample Labeling Information**

Soil/Chemical Identification	Soil Weight, g	Chemical Added, %	Chemical Weight, g	Soil pH	Sample ID#
Fort Polk/Hap	5.0	0	0.0	Natural	Samples 1, 2, 3
Fort Polk/Hap	5.0	1	0.05	Natural	Samples 1, 2, 3
Fort Polk/Hap	5.0	3	0.15	Natural	Samples 1, 2, 3
Fort Polk/Hap	5.0	5	0.25	Natural	Samples 1, 2, 3
Fort Polk/Hap	5.0	0	0.0	pH 3	Samples 1, 2, 3
Fort Polk/Hap	5.0	1	0.05	pH 3	Samples 1, 2, 3
Fort Polk/Hap	5.0	3	0.15	pH 3	Samples 1, 2, 3
Fort Polk/Hap	5.0	5	0.25	pH 3	Samples 1, 2, 3

Suggested Acronyms for Chemicals Added  
 Hydroxyapatite = Hap, Calcium Phosphate = Cap, Sodium Phosphate = Nap, Potassium Phosphate = Kap, Ammonium Phosphate = Amp, Granular Iron = Gr Fe, Colloidal iron = Co Fe

### Chemical treatment of soils at pH 3

- a.* Follow the procedures in Steps *a* through *c* of "Chemical treatment at natural soil pH."
- b.* Add 25 ml DDI water to each soil.
- c.* Add 5 ml 0.2-M Ultrex nitric acid by pipet to each bottle and place the screw caps on the bottles.
- d.* Vigorously shake the bottles, then check the pH with pH paper.
- e.* Continue with preceding Steps *c* and *d* adding acid in 1- to 2-ml increments until the pH is lowered to  $3.0 \pm 0.5$ . Record each aliquot of acid that is added to the bottle.
- f.* Place the samples on the rotary tumbler for about 10 minutes.
- g.* Measure the initial pH and ORP of the samples with the pH/ORP meter by placing the electrodes in the liquid layer of the soil mixture. Record results.

- h.* Place the samples back on the tumbler. Stop the tumbler at 24 and 48 hours and recheck the pH with pH paper. If the pH increases above 3.0, add additional acid in 1- to 2-ml increments to maintain the samples at pH 3. Record each aliquot of acid that is added to the bottle.
- i.* After adjusting the samples to  $\text{pH } 3 \pm 0.5$ , add DDI water to a total volume of 50 ml. Continue tumbling the samples for a total of  $72 \pm 2$  hours.
- j.* Follow the instructions given in *g* through *l* of "Chemical treatment at natural soil pH."

# Appendix B

## pH and Oxidation-Reduction Potential (ORP) Results

<b>Table B1 Iron-Treated Soils</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
Fort Polk (0% Treatment)	6.11	3.48	208.2	386.8
Fort Polk (1% Granular Fe)	6.04	3.59	161.2	385.2
Fort Polk (3% Granular Fe)	6.11	3.55	150.1	373.0
Fort Polk (5% Granular Fe)	6.11	3.43	217.7	461.5
Fort Polk (1% Colloidal Fe)	6.06	3.46	231.4	404.5
Fort Polk (3% Colloidal Fe)	5.99	3.61	222.0	381.7
Fort Polk (5% Colloidal Fe)	6.23	3.40	238.2	379.4
New Orleans (0% Fe)	7.50	2.85	189.9	485.7
New Orleans (1% Granular Fe)	7.58	2.54	228.9	411.6
New Orleans (3% Granular Fe)	7.76	3.08	200.1	478.2
New Orleans (5% Granular Fe)	7.61	2.86	174.2	485.0
New Orleans (1% Colloidal Fe)	5.96	3.41	379.8	431.8
New Orleans (3% Colloidal Fe)	7.58	2.77	170.4	436.5
New Orleans (5% Colloidal Fe)	7.75	2.72	152.9	430.9
Kodiak (0% Treatment)	6.19	3.95	218.1	349.1
Kodiak (1% Granular Fe)	6.17	3.14	190.1	285.5
Kodiak (3% Granular Fe)	6.20	3.33	195.3	239.8
Kodiak (5% Granular Fe)	6.16	3.46	184.3	371.4
Kodiak (1% Colloidal Fe)	6.15	3.49	185.6	387.4
Kodiak (3% Colloidal Fe)	6.18	3.55	187.5	340.6
Kodiak (5% Colloidal Fe)	6.15	3.67	187.9	354.9
WES 0ppm (0% Fe)	5.61	2.50	422.3	504.0
WES 0ppm (1% Granular Fe)	5.77	2.92	441.1	542.2
WES 0ppm (3% Granular Fe)	5.84	3.12	394.0	442.5
WES 0ppm (5% Granular Fe)	5.93	3.32	241.9	400.5
WES 0ppm (1% Colloidal Fe)	6.64	2.50	362.4	481.6
WES 0ppm (3% Colloidal Fe)	7.66	2.61	-164	441.7
WES 0ppm (5% Colloidal Fe)	7.70	2.33	-183.7	425.6
(Sheet 1 of 3)				

<b>Table B1 (Continued)</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
Kaolin 0ppm (0% Fe)	5.94	2.86	320.2	424.1
Kaolin 0ppm (1% Granular Fe)	5.99	3.01	52.1	524.1
Kaolin 0ppm (3% Granular Fe)	6.07	2.89	114.0	517.2
Kaolin 0ppm (5% Granular Fe)	6.23	2.68	53.0	432.2
Kaolin 0ppm (1% Colloidal Fe)	5.90	3.02	160.1	408.0
Kaolin 0ppm (3% Colloidal Fe)	6.83	3.87	73	345.2
Kaolin 0ppm (5% Colloidal Fe)	6.81	2.70	-71.9	454.3
WES 500ppm (0% Fe)	5.73	2.68	347	474.0
WES 500ppm (1% Granular Fe)	5.69	3.12	214.7	421.7
WES 500ppm (3% Granular Fe)	5.74	3.58	175.8	380.0
WES 500ppm (5% Granular Fe)	5.89	2.64	128.0	447.3
WES 500ppm (1% Colloidal Fe)	6.76	2.99	99.9	360.7
WES 500ppm (3% Colloidal Fe)	6.70	2.92	148.2	427.2
WES 500ppm (5% Colloidal Fe)	6.75	2.55	-31.2	375.1
WES 1000ppm (0% Fe)	5.58	2.83	203.7	590.3
WES 1000ppm (1% Granular Fe)	5.55	3.22	221.1	407.4
WES 1000ppm (3% Granular Fe)	5.57	2.55	263.1	380.7
WES 1000ppm (5% Granular Fe)	5.65	3.73	236.6	326.6
WES 1000ppm (1% Colloidal Fe)	5.62	2.56	183.2	487.0
WES 1000ppm (3% Colloidal Fe)	6.75	2.97	121.9	489.1
WES 1000ppm (5% Colloidal Fe)	6.44	2.39	-66.2	358.2
WES 2000ppm (0% Fe)	5.43	2.61	185.9	480.6
WES 2000ppm (1% Granular Fe)	5.47	3.23	240.4	430.5
WES 2000ppm (3% Granular Fe)	5.48	3.18	248.0	423.4
WES 2000ppm (5% Granular Fe)	5.55	3.51	216.2	354.4
WES 2000ppm (1% Colloidal Fe)	5.40	2.93	249.2	566.6
WES 2000ppm (3% Colloidal Fe)	6.62	3.05	122.3	443.1
WES 2000ppm (5% Colloidal Fe)	6.21	3.84	-68.8	260.0
Kaolin 500ppm (0% Fe )	5.57	3.18	278.9	409.1
Kaolin 500ppm (1% Gran Fe)	5.56	3.68	184.6	362.5
Kaolin 500ppm (3% Gran Fe)	5.72	3.39	170.1	378.5
Kaolin 500ppm (5% Gran Fe)	5.72	3.48	153.9	371.7
Kaolin 500ppm (1% Coll Fe)	5.51	3.57	244.4	349.1
Kaolin 500ppm (3% Coll Fe)	5.52	3.80	238.5	276.2
Kaolin 500ppm (5% Coll Fe)	5.32	3.54	242.7	283.6
Kaolin 1000ppm (0% Fe)	5.32	2.50	301.1	472.9
Kaolin 1000ppm (1% Gran Fe)	5.50	3.75	229.5	348.2
Kaolin 1000ppm (3% Gran Fe)	5.61	3.47	190.1	302.3
Kaolin 1000ppm (5% Gran Fe)	5.70	3.79	194.2	332.9
Kaolin 1000ppm (1% Coll Fe)	5.37	3.37	273.7	389.0
Kaolin 1000ppm (3% Coll Fe)	5.40	3.41	257.8	271.6
Kaolin 1000ppm (5% Coll Fe)	5.42	2.50	268.6	444.6
Kaolin 2000ppm (0% Fe)	5.34	3.12	268.5	434.9
Kaolin 2000ppm (1% Gran Fe)	5.45	3.09	217.5	451.3
Kaolin 2000ppm (3% Gran Fe)	5.63	2.57	175.5	470.5

(Sheet 2 of 3)

<b>Table B1 (Concluded)</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
Kaolin 2000ppm (5% Gran Fe)	5.71	3.67	176.6	342.6
Kaolin 2000ppm (1% Coll Fe)	5.34	3.20	243.4	388.6
Kaolin 2000ppm (3% Coll Fe)	5.40	3.43	259.3	273.4
Kaolin 2000ppm (5% Coll Fe)	5.38	3.35	260.7	395.4
<i>(Sheet 3 of 3)</i>				

<b>Table B2 Phosphate-Amended SAFR Soils</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
Fort Polk 0% Phosphate	5.51	2.82	265.9	485.3
Fort Polk 1% Hap-p	6.88	3.52	194.5	379.2
Fort Polk 3% Hap-p	7.09	3.78	190.7	368.3
Fort Polk 5% Hap-p	7.22	2.50	208.2	473.4
Fort Polk 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.72	3.43	220.8	357.5
Fort Polk 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.75	3.73	228.9	364.8
Fort Polk 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.80	3.20	224.7	420.8
Fort Polk 1% Na <sub>3</sub> PO <sub>4</sub>	8.24	3.71	204.8	336.3
Fort Polk 3% Na <sub>3</sub> PO <sub>4</sub>	9.47	3.38	173.8	394.3
Fort Polk 5% Na <sub>3</sub> PO <sub>4</sub>	10.50	3.00	120.8	435.7
Fort Polk 1% K <sub>3</sub> PO <sub>4</sub>	6.87	3.43	244.5	341.1
Fort Polk 3% K <sub>3</sub> PO <sub>4</sub>	6.42	3.66	272.8	308.4
Fort Polk 5% K <sub>3</sub> PO <sub>4</sub>	6.23	3.78	285.3	305.3
Fort Polk 1% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.70	3.18	257.7	375.0
Fort Polk 3% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.36	3.57	263.0	347.2
Fort Polk 5% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.17	3.55	262.3	337.5
New Orleans 0% Phosphate	7.41	2.52	368.5	468.5
New Orleans 1% Hap-p	7.44	2.98	330.2	431.4
New Orleans 3% Hap-p	7.51	2.50	336.2	235.2
New Orleans 5% Hap-p	7.54	2.66	331.7	472.6
New Orleans 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	7.66	2.70	127.2	449.9
New Orleans 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	7.67	2.59	153.2	465.5
New Orleans 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	7.68	2.48	177.4	435.6
New Orleans 1% Na <sub>3</sub> PO <sub>4</sub>	9.05	2.55	266.4	519.8
New Orleans 3% Na <sub>3</sub> PO <sub>4</sub>	10.91	2.75	132.2	458.5
New Orleans 5% Na <sub>3</sub> PO <sub>4</sub>	11.18	2.90	86.5	496.0
New Orleans 1% K <sub>3</sub> PO <sub>4</sub>	6.70	2.66	325.9	472.1
New Orleans 3% K <sub>3</sub> PO <sub>4</sub>	6.38	2.39	331.6	408.2
New Orleans 5% K <sub>3</sub> PO <sub>4</sub>	6.16	3.62	351.0	411.4
New Orleans 1% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.73	2.78	336.6	442.7
New Orleans 3% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.26	3.47	375.0	387.5
New Orleans 5% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.06	2.65	367.9	399.3
Kodiak 0% Phosphate	6.18	3.48	368.5	407.2
Kodiak 1% Hap-p	6.19	3.74	248.7	341.0
<i>(Continued)</i>				

<b>Table B2 (Concluded)</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
Kodiak 3% Hap-p	6.38	3.49	241.1	330.8
Kodiak 5% Hap-p	6.48	3.80	242.6	327.9
Kodiak 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.13	3.82	209.1	318.6
Kodiak 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.26	3.51	222.9	382.5
Kodiak 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.37	3.60	245.3	391.6
Kodiak 1% Na <sub>3</sub> PO <sub>4</sub>	7.14	3.55	173.4	325.2
Kodiak 3% Na <sub>3</sub> PO <sub>4</sub>	7.92	3.42	106.1	344.0
Kodiak 5% Na <sub>3</sub> PO <sub>4</sub>	8.35	3.29	34.2	347.2
Kodiak 1% K <sub>3</sub> PO <sub>4</sub>	6.58	3.37	226.5	318.7
Kodiak 3% K <sub>3</sub> PO <sub>4</sub>	6.33	2.91	225.1	384.3
Kodiak 5% K <sub>3</sub> PO <sub>4</sub>	6.13	3.30	229.3	300.4
Kodiak 1% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.56	3.22	217.5	319.2
Kodiak 3% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.23	2.91	226.7	366.6
Kodiak 5% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.05	3.21	275.8	313.1
Camp Keller 0% Phosphate	5.38	2.46	323.6	628.8
Camp Keller 1% Hap-p	5.94	2.84	450.1	582.7
Camp Keller 3% Hap-p	6.42	2.83	452.0	446.0
Camp Keller 5% Hap-p	6.56	3.04	487.3	435.0
Camp Keller 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	5.97	3.09	432.9	472.0
Camp Keller 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.42	2.96	444.6	400.4
Camp Keller 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.58	3.01	465.2	396.6
Camp Keller 1% K <sub>3</sub> PO <sub>4</sub>	5.73	2.80	485.2	388.3
Camp Keller 3% K <sub>3</sub> PO <sub>4</sub>	5.46	3.01	428.0	340.0
Camp Keller 5% K <sub>3</sub> PO <sub>4</sub>	5.35	2.97	436.2	342.8

<b>Table B3 Phosphate-Amended WES Soils</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
WES 0ppm 0% Phosphate	6.26	2.84	395.9	456.2
WES 0ppm 1% Hap-p	6.24	2.43	348.0	393.0
WES 0ppm 3% Hap-p	6.38	3.67	337.8	441.0
WES 0ppm 5% Hap-p	6.44	3.03	351.7	465.4
WES 0ppm 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.34	2.73	404.2	400.3
WES 0ppm 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.48	3.48	389.8	425.9
WES 0ppm 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.57	3.48	374.3	403.0
WES 0ppm 1% Na <sub>3</sub> PO <sub>4</sub>	8.01	3.42	187.3	359.7
WES 0ppm 3% Na <sub>3</sub> PO <sub>4</sub>	9.18	2.72	133.3	412.4
WES 0ppm 5% Na <sub>3</sub> PO <sub>4</sub>	10.35	3.25	49.6	191.6
WES 0ppm 1% K <sub>3</sub> PO <sub>4</sub>	5.26	3.08	376.7	406.5
WES 0ppm 3% K <sub>3</sub> PO <sub>4</sub>	5.16	3.22	374.9	400.0
WES 0ppm 5% K <sub>3</sub> PO <sub>4</sub>	5.12	3.28	376.0	402.8
WES 0ppm 1% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.34	3.09	400.8	385.7
WES 0ppm 3% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.09	3.37	410.4	380.0
<i>(Sheet 1 of 3)</i>				

<b>Table B3 (Continued)</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
WES 0ppm 5% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.17	3.23	392.9	381.5
WES 500ppm 0% Phosphate	6.54	2.79	441.7	468.5
WES 500ppm 1% Hap-p	6.15	3.55	124.4	320.7
WES 500ppm 3% Hap-p	6.27	3.60	134.7	406.1
WES 500ppm 5% Hap-p	6.30	3.47	155.7	409.9
WES 500ppm 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.08	2.75	144.9	394.4
WES 500ppm 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.22	3.35	154.5	421.5
WES 500ppm 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.35	2.99	115.8	438.6
WES 500ppm 1% Na <sub>3</sub> PO <sub>4</sub>	9.41	3.01	80.3	464.7
WES 500ppm 3% Na <sub>3</sub> PO <sub>4</sub>	10.05	3.66	61.3	427.8
WES 500ppm 5% Na <sub>3</sub> PO <sub>4</sub>	10.54	3.16	33.0	427.0
WES 500ppm 1% K <sub>3</sub> PO <sub>4</sub>	5.54	3.18	167.9	374.3
WES 500ppm 3% K <sub>3</sub> PO <sub>4</sub>	5.45	3.25	227.9	373.0
WES 500ppm 5% K <sub>3</sub> PO <sub>4</sub>	5.27	3.39	241.7	353.8
WES 500ppm 1% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.69	3.21	134.9	361.4
WES 500ppm 3% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.45	3.29	169.0	362.2
WES 500ppm 5% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.30	3.42	229.9	365.0
WES 1000ppm 0% Phosphate	6.03	2.60	409.5	512.0
WES 1000ppm 1% Hap-p	7.29	2.43	399.5	385.0
WES 1000ppm 3% Hap-p	6.41	3.31	379.2	457.0
WES 1000ppm 5% Hap-p	6.40	3.47	377.5	449.4
WES 1000ppm 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.22	3.07	371.9	302.6
WES 1000ppm 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.38	3.52	357.5	420.4
WES 1000ppm 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.47	3.49	334.5	436.0
WES 1000ppm 1% Na <sub>3</sub> PO <sub>4</sub>	7.76	3.32	294.4	272.1
WES 1000ppm 3% Na <sub>3</sub> PO <sub>4</sub>	9.06	2.80	200.7	400.7
WES 1000ppm 5% Na <sub>3</sub> PO <sub>4</sub>	10.71	3.10	62.7	403.4
WES 1000ppm 1% K <sub>3</sub> PO <sub>4</sub>	5.26	2.67	241.2	375.7
WES 1000ppm 3% K <sub>3</sub> PO <sub>4</sub>	5.29	2.84	243.1	370.7
WES 1000ppm 5% K <sub>3</sub> PO <sub>4</sub>	5.18	2.90	267.2	375.3
WES 1000ppm 1% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.30	2.66	257.4	348.6
WES 1000ppm 3% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.25	2.85	259.7	361.4
WES 1000ppm 5% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.21	2.91	267.3	359.1
WES 2000ppm 0% Phosphate	6.41	2.76	392.3	483.4
WES 2000ppm 1% Hap-p	6.18	3.26	242.4	395.5
WES 2000ppm 3% Hap-p	6.33	3.02	235.9	352.9
WES 2000ppm 5% Hap-p	6.39	3.56	208.8	434.1
WES 2000ppm 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.22	3.40	224.8	459.4
WES 2000ppm 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.26	2.28	220.8	325.6
WES 2000ppm 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.44	3.47	224.2	343.1
WES 2000ppm 1% Na <sub>3</sub> PO <sub>4</sub>	7.28	3.31	182.2	373.0
WES 2000ppm 3% Na <sub>3</sub> PO <sub>4</sub>	9.37	2.99	125.1	416.2
WES 2000ppm 5% Na <sub>3</sub> PO <sub>4</sub>	10.66	3.17	42.2	414.7
WES 2000ppm 1% K <sub>3</sub> PO <sub>4</sub>	5.50	2.71	115.9	365.4
WES 2000ppm 3% K <sub>3</sub> PO <sub>4</sub>	5.23	2.84	218.1	359.7
(Sheet 2 of 3)				

<b>Table B3 (Concluded)</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
WES 2000ppm 5% K3PO4	5.17	2.96	239.0	358.9
WES 2000ppm 1% (NH4)3PO4	5.41	2.64	241.5	385.4
WES 2000ppm 3% (NH4)3PO4	5.28	2.86	247.5	379.7
WES 2000ppm 5% (NH4)3PO4	5.36	3.05	262.3	371.6
<i>(Sheet 3 of 3)</i>				

<b>Table B4 Phosphate-Amended Kaolin Soils</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
Kaolin Oppm 0% Phosphate	6.51	2.88	371.5	431.8
Kaolin Oppm 1% Hap-p	6.72	3.10	374.5	273.8
Kaolin Oppm 3% Hap-p	6.66	3.59	356.8	296.8
Kaolin Oppm 5% Hap-p	6.69	2.51	434.2	389.2
Kaolin Oppm 1% Ca3(PO4)2	6.57	2.92	390.8	369.6
Kaolin Oppm 3% Ca3(PO4)2	6.55	3.32	408.2	361.2
Kaolin Oppm 5% Ca3(PO4)2	6.57	2.98	425.7	445.3
Kaolin Oppm 1% Na3PO4	8.79	3.08	90.0	305.0
Kaolin Oppm 3% Na3PO4	10.96	2.58	-4.5	355.3
Kaolin Oppm 5% Na3PO4	11.49	3.44	-6.1	349.6
Kaolin Oppm 1% K3PO4	5.96	2.93	368.7	294.0
Kaolin Oppm 3% K3PO4	5.74	2.97	365.8	293.7
Kaolin Oppm 5% K3PO4	5.59	3.06	406.4	295.6
Kaolin Oppm 1% (NH4)3PO4	5.83	3.45	437.1	319.1
Kaolin Oppm 3% (NH4)3PO4	5.62	3.10	383.8	311.3
Kaolin Oppm 5% (NH4)3PO4	5.52	3.19	404.1	309.1
Kaolin 500ppm 0% Phosphate	6.54	2.95	348.2	436.3
Kaolin 500ppm 1% Hap-p	6.41	2.86	393.5	271.2
Kaolin 500ppm 3% Hap-p	6.62	3.43	426.9	383.5
Kaolin 500ppm 5% Hap-p	6.74	3.49	419.4	350.7
Kaolin 500ppm 1% Ca3(PO4)2	6.48	2.91	410.9	377.4
Kaolin 500ppm 3% Ca3(PO4)2	6.61	3.41	375.9	355.6
Kaolin 500ppm 5% Ca3(PO4)2	6.68	2.44	385	432.7
Kaolin 500ppm 1% Na3PO4	10.18	3.18	162.0	311.9
Kaolin 500ppm 3% Na3PO4	10.71	3.18	41.6	351.3
Kaolin 500ppm 5% Na3PO4	11.39	2.87	15.2	384.1
Kaolin 500ppm 1% K3PO4	6.16	3.25	364.7	332.0
Kaolin 500ppm 3% K3PO4	5.89	3.40	372.3	342.7
Kaolin 500ppm 5% K3PO4	5.75	3.47	370.4	355.2
Kaolin 500ppm 1% (NH4)3PO4	6.13	3.27	403.0	302.9
Kaolin 500ppm 3% (NH4)3PO4	5.85	3.50	402.6	291.8
Kaolin 500ppm 5% (NH4)3PO4	5.69	3.49	380.3	286.1
Kaolin 1000ppm 0% Phosphate	6.53	2.92	358.9	462.2
Kaolin 1000ppm 1% Hap-p	6.36	3.51	372.3	341.7
Kaolin 1000ppm 3% Hap-p	6.62	3.32	342.3	373.1
<i>(Continued)</i>				



<b>Table B4 (Concluded)</b>				
<b>Soil Identification and Treatment</b>	<b>Natural pH</b>	<b>Adjusted pH</b>	<b>Natural ORP, mV</b>	<b>ORP after pH Adjustment, mV</b>
Kaolin 1000ppm 5% Hap-p	6.71	3.44	358.4	394.9
Kaolin 1000ppm 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.47	3.57	351.5	315.5
Kaolin 1000ppm 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.61	2.90	345.8	344.7
Kaolin 1000ppm 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.74	3.49	350.3	360.9
Kaolin 1000ppm 1% Na <sub>3</sub> PO <sub>4</sub>	8.47	3.31	117.3	303.6
Kaolin 1000ppm 3% Na <sub>3</sub> PO <sub>4</sub>	10.86	2.55	70.9	365.8
Kaolin 1000ppm 5% Na <sub>3</sub> PO <sub>4</sub>	11.52	2.37	3.4	376.8
Kaolin 1000ppm 1% K <sub>3</sub> PO <sub>4</sub>	5.94	2.99	362.1	407.7
Kaolin 1000ppm 3% K <sub>3</sub> PO <sub>4</sub>	5.72	3.13	343.5	406.6
Kaolin 1000ppm 5% K <sub>3</sub> PO <sub>4</sub>	5.59	3.28	359.8	416.6
Kaolin 1000ppm 1% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.95	2.99	369.9	411.6
Kaolin 1000ppm 3% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.67	3.27	360.0	347.5
Kaolin 1000ppm 5% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.54	2.84	208.2	393.0
Kaolin 2000ppm 0% Phosphate	6.49	2.98	376.2	478.1
Kaolin 2000ppm 1% Hap-p	6.84	3.14	208.2	330.7
Kaolin 2000ppm 3% Hap-p	6.80	3.18	203.0	405.9
Kaolin 2000ppm 5% Hap-p	6.88	3.49	190.7	346.8
Kaolin 2000ppm 1% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.07	3.49	345.0	375.0
Kaolin 2000ppm 3% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.61	3.55	326.2	305.7
Kaolin 2000ppm 5% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.66	3.66	330.0	320.6
Kaolin 2000ppm 1% Na <sub>3</sub> PO <sub>4</sub>	8.35	3.14	126.1	328.9
Kaolin 2000ppm 3% Na <sub>3</sub> PO <sub>4</sub>	10.49	2.72	44.0	360.6
Kaolin 2000ppm 5% Na <sub>3</sub> PO <sub>4</sub>	11.02	3.45	45.0	350.8
Kaolin 2000ppm 1% K <sub>3</sub> PO <sub>4</sub>	5.84	2.99	377.5	374.5
Kaolin 2000ppm 3% K <sub>3</sub> PO <sub>4</sub>	5.64	3.17	361.7	392.0
Kaolin 2000ppm 5% K <sub>3</sub> PO <sub>4</sub>	5.61	3.20	378.8	352.4
Kaolin 2000ppm 1% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.21	3.08	360.5	335.3
Kaolin 2000ppm 3% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	6.13	3.25	358.7	332.4
Kaolin 2000ppm 5% (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	5.55	3.30	354.5	342.2

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<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> <p>The U.S. military operates Small Arms Firing Ranges (SAFRs) at various locations in and outside the United States. The ranges are used for munitions training for military personnel. Because the ranges have been in operation for a number of years, the soils at SAFRs are contaminated with spent munitions, lead bullets, and other metal contaminants. Although SAFR projectiles contain primarily lead, copper, and antimony, lead is by far the most toxic component. As a consequence of lead-contaminated soils and the distinctive site topographies found at SAFRs, the potential for lead migration that poses risks to the environment exists. Remediation efforts are needed to mitigate lead mobility and availability.</p> <p>Numerous studies have been conducted on reducing the impact of lead contaminants in the environment. This study tests chemical materials for lead stabilization that are economical and readily adaptable to field application at SAFRs. The study evaluates the effectiveness of iron and phosphate chemicals as in situ treatments for reducing lead mobility at SAFRs.</p> <p>Two leaching tests were developed. One test evaluated treatment effectiveness during leaching at the natural soil pH, and the second leach test was conducted at a lower, acidic, pH to estimate the long-term effects of lead leaching at SAFRs.</p> <p>The study showed that phosphate amendments were more effective than iron amendments in stabilizing lead in SAFR soils.</p>					
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